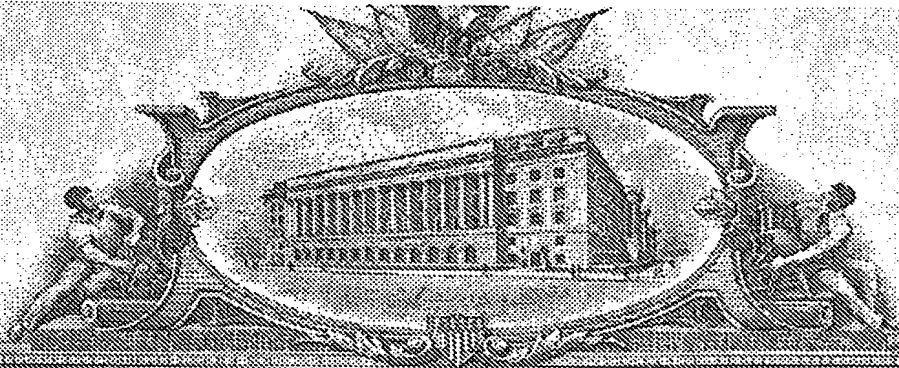


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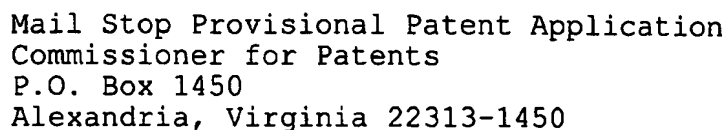
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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[] Additional inventors are being named on the _____
separately numbered sheet(s) attached hereto.

Title of the Invention: PLATINUM-COPPER FUEL CELL ELECTROCATALYST

Correspondence Address: Customer Number 000321

ENCLOSED APPLICATION PARTS:

- ☒ Specification - Number of Pages 48
- ☒ Drawings - Number of Sheets 4
- ☒ Application Data Sheet
- ☐ CD(s), Number
- ☒ Return Receipt Postcard
- ☐ Other (specify) _____


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- ☐ Applicant claims small entity status
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

- ☒ No
- ☐ Yes, the name of the U.S. Government agency and the Government contract number are: _____

Respectfully submitted,


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Date: August 18, 2003

SMR/cak/msc

PLATINUM-COPPER FUEL CELL ELECTROCATALYST

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] The present invention relates to electrocatalysts, especially to platinum-copper electrocatalysts, which are useful in fuel cell electrodes and other electrocatalytic structures.

DESCRIPTION OF RELATED TECHNOLOGY

[0002] A fuel cell is an electrochemical device for directly converting the chemical energy generated from an oxidation-reduction reaction of a fuel such as hydrogen or hydrocarbon-based fuels and an oxidizer such as oxygen gas (in air) supplied thereto into a low-voltage direct current. Thus, fuel cells chemically combine the molecules of a fuel and an oxidizer without burning, dispensing with the inefficiencies and pollution of traditional combustion.

[0003] A fuel cell is generally comprised of a fuel electrode (anode), an oxidizer electrode (cathode), an electrolyte interposed between the electrodes (alkaline or acidic), and means for separately supplying a stream of fuel and a stream of oxidizer to the anode and the cathode, respectively. In operation, fuel supplied to the anode is oxidized, releasing electrons that are conducted via an external circuit to the cathode. At the cathode, the supplied electrons are consumed when the oxidizer is reduced. The current flowing through the external circuit can be made to do useful work.

[0004] There are several types of fuel cells, including those having electrolytes of: phosphoric acid, molten carbonate, solid oxide, potassium hydroxide, and proton exchange membrane. A phosphoric acid fuel cell operates at about 160-220 °C, and preferably at about 190-200 °C. This type of fuel cell is currently being used for multi-megawatt utility power generation and for co-generation systems (i.e., combined heat and power generation) in the 50 to several hundred kilowatts range.

[0005] In contrast, proton exchange membrane fuel cells use a solid proton-conducting polymer membrane as the electrolyte. Typically, the polymer membrane is maintained in a hydrated form during operation in order to prevent loss of ionic conduction which limits the operation temperature typically to between about 70 and about 120 °C depending on the operating pressure, and preferably below about

100 °C. Proton exchange membrane fuel cells have a much higher power density than liquid electrolyte fuel cells (e.g., phosphoric acid), and can vary output quickly to meet shifts in power demand. Thus, they are suited for applications such as in automobiles and small-scale residential power generation where quick startup is a consideration.

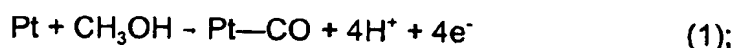
[0006] In some applications (e.g., automotive) pure hydrogen gas is the optimum fuel; however, in other applications where a lower operational cost is desirable, a reformed hydrogen-containing gas is an appropriate fuel. A reformed-hydrogen containing gas is produced, for example, by steam-reforming methanol and water at 200-300 °C to a hydrogen-rich fuel gas containing carbon dioxide. Theoretically, the reformat gas consists of 75 vol% hydrogen and 25 vol% carbon dioxide. In practice, however, this gas also contains nitrogen, oxygen, and, depending on the degree of purity, varying amounts of carbon monoxide (up to 1 vol%). Although some electronic devices also reform liquid fuel to hydrogen, in some applications the conversion of a liquid fuel directly into electricity is desirable, as then a high storage density and system simplicity are combined. In particular, methanol is an especially desirable fuel because it has a high energy density, a low cost, and is produced from renewable resources.

[0007] For the oxidation and reduction reactions in a fuel cell to proceed at useful rates, especially at operating temperatures below about 300 °C, electrocatalyst materials are typically provided at the electrodes. Initially, fuel cells used electrocatalysts made of a single metal, usually platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), osmium (Os), silver (Ag) or gold (Au) because they are able to withstand the corrosive environment - platinum being the most efficient and stable single-metal electrocatalyst for fuel cells operating below about 300 °C. While these elements were first used in fuel cells in metallic powder form, later techniques were developed to disperse these metals over the surface of electrically conductive supports (e.g., carbon black) to increase the surface area of the electrocatalyst which in turn increased the number of reactive sites leading to improved efficiency of the cell. Nevertheless, fuel cell performance typically declines over time because the presence of electrolyte, high temperatures and molecular oxygen dissolve the electrocatalyst and/or sinter the dispersed electrocatalyst by surface migration or dissolution/re-precipitation.

[0008] Although platinum is the most efficient and stable single-metal electrocatalyst for fuel cells, it is costly and an increase in electrocatalyst activity over platinum is necessary for wide scale commercialization of fuel cell technology. The development of cathode fuel cell electrocatalyst materials faces longstanding challenges. The greatest challenge is the improvement of the electrode kinetics of

the oxygen reduction reaction. In fact, sluggish electrochemical reaction kinetics have prevented attaining the thermodynamic reversible electrode potential for oxygen reduction. This is reflected in exchange current densities of around 10^{-10} to 10^{-12} A/cm² for oxygen reduction on, for example, Pt at low and medium temperatures. A factor contributing to this phenomenon includes the fact that the desired reduction of oxygen to water is a four-electron transfer reaction and typically involves breaking a strong O-O bond early in the reaction. In addition, the open circuit voltage is lowered from the thermodynamic potential for oxygen reduction due to the formation of peroxide and possible platinum oxides that inhibit the reaction. A second challenge is the stability of the oxygen electrode (cathode) during long-term operation. Specifically, a fuel cell cathode operates in a regime in which even the most unreactive metals are not completely stable. Thus, alloy compositions that contain non-noble metal elements may have a rate of corrosion that would negatively impact the projected lifetime of a fuel cell. The corrosion may be more severe when the cell is operating near open circuit conditions (which is the most desirable potential for thermodynamic efficiency).

[0009] Electrocatalyst materials at the anode also face challenges during fuel cell operation. Specifically, as the concentration of carbon monoxide (CO) rises above about 10 ppm in the fuel the surface of the electrocatalyst can be rapidly poisoned. As a result, platinum (by itself) is a poor electrocatalyst if the fuel stream contains carbon monoxide (e.g., reformed-hydrogen gas typically exceeds 100 ppm). Liquid hydrocarbon-based fuels (e.g., methanol) present an even greater poisoning problem. Specifically, the surface of the platinum becomes blocked with the adsorbed intermediate, carbon monoxide (CO). It has been reported that H₂O plays a key role in the removal of such poisoning species in accordance with the following reactions:



As indicated by the foregoing reactions, the methanol is adsorbed and partially oxidized by platinum on the surface of the electrode (1). Adsorbed OH, from the hydrolysis of water, reacts with the adsorbed CO to produce carbon dioxide and a proton (2,3). However, platinum does not form OH species well at the potentials fuel cell electrodes operate (e.g., 200 mV-1.5 V). As a result, step (3) is the slowest step in the sequence, limiting the rate of CO removal, thereby allowing poisoning of the electrocatalyst to occur. This applies in particular to a proton exchange membrane

fuel cell which is especially sensitive to CO poisoning because of its low operating temperatures.

[0010] One technique for increasing electrocatalytic cathodic activity during the reduction of oxygen and electrocatalytic anodic activity during the oxidation of hydrogen is to employ an electrocatalyst which is more active, corrosion resistant, and/or more poison tolerant. For example, increased tolerance to CO has been reported by alloying platinum and ruthenium at a 50:50 atomic ratio (see, D. Chu and S. Gillman, J. Electrochem. Soc. 1996, 143, 1685). The electrocatalysts proposed to date, however, leave room for further improvement.

BRIEF SUMMARY OF THE INVENTION

[0011] Briefly, therefore, the present invention is directed to a supported metal alloy powder, the supported metal alloy powder comprising metal alloy deposits on electrically conductive supports, wherein the metal alloy deposits comprise platinum and copper, a concentration of copper that is greater than 50 atomic percent, and an average size that is no greater than about 30 Å.

[0012] The present invention is also directed to a supported metal alloy powder, the supported metal alloy powder comprising wherein the metal alloy deposits comprise platinum and copper, a lattice parameter that is no more than 3.777 Å, and an average size that is no greater than about 30 Å.

[0013] The present invention is also directed to a fuel cell electrode, the fuel cell electrode comprising one of the two foregoing supported metal alloy powders and an electrode substrate upon which the supported electrocatalyst powder is deposited.

[0014] Additionally, the present invention is directed to a fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and a catalyst for the catalytic oxidation of a hydrogen-containing fuel or the catalytic reduction of oxygen, the catalyst comprising an alloy comprising platinum and copper, wherein the concentration of copper in the alloy is greater than 50 atomic percent.

[0015] Further, the present invention is directed to a method for the electrochemical conversion of a hydrogen-containing fuel and oxygen to reaction products and electricity in the foregoing fuel cell, and an electrically conductive external circuit connecting the anode and cathode, the method comprising contacting the hydrogen-containing fuel or the oxygen and the catalyst to catalytically oxidize the hydrogen-containing fuel or catalytically reduce the oxygen.

[0016] The present invention is also directed to an unsupported catalyst layer on a surface of an electrolyte membrane or an electrode, said unsupported catalyst layer comprising platinum and copper, wherein the concentration of copper is greater than 50 atomic percent.

[0017] The foregoing and other features and advantages of the present invention will become more apparent from the following description and accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Figure 1 is a TEM image of a carbon support with platinum-copper alloy nanoparticles deposited thereon in accordance with an embodiment of the present invention.

[0019] Figure 2 is a schematic structural view showing essential members of a fuel cell.

[0020] Figure 3 is a side view of a fuel cell.

[0021] Figure 4 is a photograph of an electrode array comprising thin-film alloy compositions deposited on individually addressable electrodes.

[0022] Figure 5 is a X-ray Diffraction plot of a supported platinum-copper alloy powder comprising carbon supports with platinum-copper alloy nanoparticles deposited on the carbon supports such as in Figure 1.

DETAILED DESCRIPTION OF THE INVENTION

Catalyst Composition

[0023] The present invention is directed to a metal-containing substance having electrocatalytic activity for use in, for example, polyelectrolyte membrane fuel cell (e.g., an electrocatalyst). In one embodiment the metal-containing substance is an alloy of the components. However, it is to be noted that the substance (e.g., electrocatalyst) may be a mixture of discrete amounts of the components (e.g., a mixture of metal powders or a mixture of deposits), wherein a discrete amount of the components may comprise a single component or a combination of components (e.g., an alloy).

[0024] In general, it is desirable to decrease the concentration of noble metals (especially platinum) to reduce the cost of an electrocatalyst. Typically, however, as the concentrations of noble metals are decreased, an electrocatalyst may become more susceptible to corrosion, and/or the activity may be diminished.

Thus, it is desirable to achieve the most activity per weight percent of noble metals without compromising, for example, the life cycle of the fuel cell in which the electrocatalyst is placed (see, e.g., end current density / weight fraction of platinum as set forth in Tables A and B, *infra*). Additionally, the composition of the present invention is preferably optimized to limit noble metal concentration while improving corrosion resistance and/or activity, as compared to platinum (e.g., at least a 3 times increase in electrocatalytic activity compared to platinum).

[0025] The present invention is thus directed to a metal-containing substance (e.g., a mixture of metal powders, deposits, or alloys) that comprises platinum and copper. Furthermore, the metal-containing substance of the present invention contains amounts of platinum and copper that are sufficient for the metals to play a role in the catalytic activity and/or crystallographic structure of the alloy. Stated another way, the concentrations of platinum and copper are such that the presence of the metals would not be considered an impurity. For example, the concentrations of each of platinum and copper are at least about 0.1, 0.5, 1, or even 2 atomic percent.

[0026] Advantageously and surprisingly, it has been discovered that catalyst compositions comprising platinum and copper (e.g., alloys) that have substantially reduced amounts of platinum are electrocatalytically active (e.g., enabling the reduction of oxygen at a fuel cell cathode) and are resistant to corrosion in acidic environments (e.g., humidified sulfonated proton conductive polymer and H_2SO_4) such as found in fuel cells. In one embodiment of the present invention the catalyst comprises a concentration of copper that is greater than 50 atomic percent. In another embodiment the concentration of copper is at least about 55 atomic percent. In yet another embodiment the concentration of copper is at least about 60 atomic percent. In still another embodiment the concentration of copper is at least about 65 atomic percent. In another embodiment the concentration of copper is no greater than about 90 atomic percent. In yet another embodiment the concentration of copper is no greater than about 85 atomic percent. In still another embodiment the concentration of copper is no greater than about 80 atomic percent. In another embodiment the concentration of copper is no greater than about 75 atomic percent. Accordingly, the concentration of copper may, in some embodiments be greater than 50 and less than about 90 atomic percent, between about 55 and about 85 atomic percent, between about 60 and about 80 atomic percent, and between about 65 and about 75 atomic percent.

[0027] In one embodiment the catalyst of the present invention comprises at least about 5 atomic percent of platinum. In other embodiments the concentration of platinum is at least about 10, 15, 20, 25, 30, 35, 40, or 45 atomic percent. In

another embodiment of the present invention the concentration of platinum is less than 50 atomic percent. In yet another embodiment the concentration of platinum is no more than about 45 atomic percent. In still another embodiment the concentration of platinum is no more than about 40 atomic percent. In another embodiment the concentration of platinum is no more than about 35 atomic percent. Accordingly, the concentration of platinum may, in some embodiments, be at least about 10 and less than 50 atomic percent, between about 15 atomic percent and 45 atomic percent, between about 20 and about 40 atomic percent, and between about 25 and about 35 atomic percent.

[0028] In view of the foregoing, in one embodiment the catalyst comprises a concentration of platinum that is at least about 10 and less than 50 atomic percent and a concentration of copper that is greater than 50 atomic percent and less than about 90 atomic percent. In another embodiment the catalyst comprises a concentration of platinum that is between about 15 and about 45 atomic percent and a concentration of copper that is between about 55 and about 85 atomic percent. In yet another embodiment the catalyst comprises a concentration of platinum that is between about 20 and about 40 atomic percent and a concentration of copper that is between about 60 and about 80 atomic percent. In still another embodiment the concentration of platinum is between about 25 and about 35 atomic percent and the concentration of copper is between about 65 and about 75 atomic percent.

[0029] In this regard it is to be noted that in one embodiment the substance of the present invention consists essentially of the platinum and copper (e.g., impurities that play little if any role in the catalytic activity and/or crystallographic structure of the catalyst may be present to some degree) and the concentrations of platinum and/or copper are in accordance with any one of the above-described embodiments. Stated another way, the concentration of a metallic or non-metallic element other than platinum and copper does not exceed what would be considered an impurity (e.g., less than 2, 1, 0.5, 0.1 atomic percent, or less). However, in other embodiments it is possible that the substance may comprise other constituents as intentional additions. For example, many metal alloys may comprise oxygen and/or carbon, either as an impurity or as a desired alloy constituent. In view of the foregoing, the catalysts/alloys of the present invention, while maintaining the same relative amounts of the constituents disclosed herein (i.e., platinum and copper), may comprise less than 100 percent of platinum and copper. Thus, in several embodiments of the present invention the total concentration of the copper and platinum atoms is greater than about 70, 80, 90, 95, or 99 atomic percent of the substance (e.g., electrocatalyst alloy).

[0030] The foregoing alloy compositions of the present invention are the overall stoichiometries, or bulk stoichiometries, of a prepared electrocatalyst prior to being subjected to an electrocatalytic reaction. That is, a reported alloy composition is an average stoichiometry over the entire volume of the prepared electrocatalyst composition, and therefore, localized stoichiometric variations may exist. For example, the volume of an electrocatalyst alloy particle comprising the surface and the first few atomic layers inward therefrom may differ from the bulk stoichiometry. Likewise, within the bulk of the particle there may be stoichiometric variations. The surface stoichiometry corresponding to a particular bulk stoichiometry is highly dependant upon the method and conditions under which the electrocatalyst alloy is prepared and alloys having the same bulk stoichiometry may have significantly different surface stoichiometries. Without being bound to a particular theory, it is believed the differing surface stoichiometries are due at least in part to differences in the atomic arrangements, chemical phases and homogeneity of the electrocatalysts.

Alloy Lattice Parameters

[0031] An electrocatalyst alloy in accordance with one or more embodiments of the present invention, may also be characterized by its lattice parameter. Specifically, a change in a lattice parameter may be indicative of a resulting change in the size of the respective metal constituents. For example, the 12-coordinate metallic radii of platinum and copper are 1.387 Å and 1.278 Å, respectively. As one metal is substituted for another, the average metal radius and, consequently, the observed lattice parameter may be expected to shrink or expand accordingly. Thus, the average radius may be used as an indicator of lattice changes as a function of stoichiometry, or alternatively, as an indicator of stoichiometry based on observed lattice parameters. It should be noted, however, that while average radii may be useful as a general rule, actual measurements should be expected to conform only in a general manner because local ordering, significant size disparity between atoms, significant changes in symmetry, and/or other factors may produce values that are inconsistent with expectations. Occasionally, the use of alternative metallic radii may be useful. One such alternative radius concept approximates metal radii using known crystallographically ordered Pt-based alloys such as PtCu (cubic symmetry is maintained) instead of pure metals. In this case, the same close-packed geometric arguments are relevant with the exception that the lattice parameter of the ordered metal alloy is used in conjunction with the accepted 12-coordinate metallic radius of platinum. According to the alternative radius concept, it is believed that the effective radius of copper is about 1.284 Å.

[0032] In one embodiment of the present invention the catalyst comprises an platinum-copper alloy having a lattice parameter no more than 3.777 Å, which is believed to generally correspond to an alloy comprising at least 50 atomic percent copper. In another embodiment the catalyst alloy has a lattice parameter of between about 3.674 and about 3.765 Å, which is believed to generally correspond to an alloy comprising between about 15 and about 45 atomic percent platinum and between about 55 and about 85 atomic percent copper. In yet another embodiment the catalyst alloy has a lattice parameter of about 3.689 and about 3.750 Å, which is believed to generally correspond to an alloy comprising between about 20 and about 40 atomic percent platinum and between about 60 and about 80 atomic percent copper. In still another embodiment the catalyst alloy has a lattice parameter of between about 3.704 and about 3.745 Å, which is believed to generally correspond to an alloy comprising between about 25 and about 35 atomic percent platinum and between about 65 and about 75 atomic percent copper.

Formation of an Electrocatalyst Alloy

[0033] The electrocatalyst alloys of the present invention may be formed by a variety of methods. For example, the appropriate amounts of the constituents may be mixed together and heated to a temperature above the respective melting points to form a molten solution of the metals that is cooled and allowed to solidify. Typically, electrocatalysts are used in a powder form to increase the surface area which increases the number of reactive sites and leads to improved efficiency of the cell. Thus, the formed metal alloy may be transformed into a powder after being solidified (e.g., by grinding) or during solidification (e.g., spraying molten alloy and allowing the droplets to solidify). It may, however, be advantageous to evaluate alloys for electrocatalytic activity in a non-powder form (see, Examples 1 and 2, *infra*).

[0034] To further increase surface area and efficiency, an electrocatalyst alloy for use in a fuel cell may be deposited over the surface of electrically conductive supports (e.g., carbon black). One method for loading an electrocatalyst alloy onto supports typically comprises depositing metal precursor compounds onto the supports, and converting the precursor compounds to metallic form and alloying the metals using a heat-treatment in a reducing atmosphere (e.g., an atmosphere comprising an inert gas such as argon). One method for depositing the precursor compounds involves chemical precipitation of precursor compounds onto the supports. The chemical precipitation method is typically accomplished by mixing supports and sources of the precursor compounds (e.g., an aqueous solution

comprising one or more inorganic metal salts) at a concentration sufficient to obtain the desired loading of the electrocatalyst on the supports and then precipitation of the precursor compounds is initiated (e.g., by adding an ammonium hydroxide solution). The slurry is then typically filtered from the liquid under vacuum, washed with deionized water, and dried to yield a powder that comprises the precursor compounds on the supports.

[0035] Another method for depositing the precursor compounds comprises forming a suspension comprising a solution and supports suspended therein, wherein the solution comprises a solvent portion and a solute portion that comprises the constituents of the precursor compound(s) being deposited. The suspension is frozen to deposit (e.g., precipitate) the precursor compound(s) on the particles. The frozen suspension is freeze-dried to remove the solvent portion and leave a freeze-dried powder comprising the supports and the deposits of the precursor compound(s) on the supports.

[0036] The solution in which the supports are dispersed/suspended provides the means for delivering the metal species which is to be deposited onto the surfaces of the supports. The metal species may be the final desired form, but in many instances it is not. If the metal species is not a final desired form, the deposited metal species is a precursor of the final desired form. Examples of such precursors or metal species include inorganic and organic metal compounds such as metal halides, sulfates, carbonates, nitrates, nitrites, oxalates, acetates, formates, etc. The conversion to the final desired form may be made by thermal decomposition, chemical reduction, or other reaction. Thermal decomposition, for example, is brought about by heating a precursor to obtain a different solid material and a gaseous material. In general, as is known, thermal decomposition of halides, sulfates, carbonates, nitrates, nitrites, oxalates, acetates, and formates may be carried out at temperatures between about 200 and about 1,200°C.

[0037] Since the process may involve sublimation of the solvent portion from the frozen suspension, the solvent portion of the solution in which the supports are suspended preferably has an appreciable vapor pressure below its freezing point. Examples of such sublimable solvents that also dissolve many metal-containing compounds and metals include water, alcohols (e.g., methanol, ethanol, etc.), acetic acid, carbon tetrachloride, ammonia, 1,2 dichloroethane, N,N-dimethylformamide, formamide, etc.

[0038] A precursor is usually selected such that any unwanted by-products from the conversion can be removed from the powder product. For example, during thermal decomposition the unwanted decomposition products are typically volatilized. To yield a final product that is an electrocatalyst metal alloy, the metal

precursors are typically selected so that the powder comprising the deposited precursors may be reduced without significantly altering the uniformity of the metal deposits on the surface of the supports and/or without significantly altering the particle size of the final powder (e.g., through agglomeration).

[0039] Nearly any metal may be deposited onto supports by the process of the present invention, provided that the metal or compound containing the metal is capable of being dissolved in a suitable medium (*i.e.*, a solvent). Likewise, nearly any metal may be combined with, or alloyed with, any other metal provided the metals or metal-containing compounds are soluble in a suitable medium.

[0040] The solute portion may comprise an organometallic compound and/or an inorganic metal-containing compound as a source of the metal species being deposited. In general, organometallic compounds are more costly, contain more impurities than inorganic metal-containing compounds, and require organic solvents. Organic solvents are more costly than water and typically require procedures and/or treatments to control purity or negate toxicity. As such, organometallic compounds and organic solvents are generally not preferred. An example of an appropriate the inorganic-copper containing compound is copper (II) nitrate. The foregoing compound is highly soluble in water; in this embodiment water is the preferred solvent. In some instances, it is desirable for an inorganic metal-containing compound to be dissolved in an acidic solution prior to being mixed with other inorganic metal-containing compounds..

[0041] To form an alloy having a particular composition or stoichiometry, the amounts of the various metal-containing source compounds necessary to achieve that composition are determined. If the supports have a pre-deposited metal, the loading of the pre-deposited metal on the supports is typically taken into account when calculating the necessary amounts of metal-containing source compounds. After the appropriate amounts of the metal-containing compounds are determined, the solution may be prepared by any appropriate method. For example, if all the selected metal-containing source compounds are soluble at the desired concentration in the same solvent at room temperature, they may merely be mixed with the solvent. Alternatively, the suspending solution may be formed by mixing source solutions, wherein a source solution comprises a particular metal-containing source compound at a particular concentration. If, however, all the selected compounds are not soluble at the same temperature when mixed together (either as powders into the solvent or as source solutions), the temperature of the mixture may be increased to increase the solubility limit of one or more of the source compounds so that the suspending solution may be formed. In addition to adjusting solubility with temperature, the stability of the suspending solution may be adjusted, for

example, by the addition of a buffer, by the addition of a complexing agent, and/or by adjusting the pH.

[0042] In addition to varying the amounts of the various metals to form alloys having different compositions, the method of the present invention allows for a wide variation in the loading of the metal onto the supports. This is beneficial because it allows for the electrocatalytic activity of a supported metal alloy powder to be maximized. The loading is controlled in part by adjusting the total concentration of the various metals in the solution while maintaining the relative amounts of the various metals. In fact, the concentrations of the inorganic metal-containing compounds may approach the solubility limit for the solution. Typically, however, the total concentration of inorganic metal-containing compounds in the solution is between about 0.01 and about 5 M which is well below the solubility limit. In one embodiment the total concentration of inorganic metal-containing compounds in the solution is between about 0.1 and about 1 M. Concentrations below the solubility limit are used because it is desirable to maximize the loading of the supported metal alloy electrocatalysts without decreasing the surface area of the metal deposits. Depending, for example, on the particular composition, the size of the deposits, and the uniformity of the deposit distribution on the supports, this maximized condition is typically achieved at a loading between about 5 and about 60 weight percent. In one embodiment the loading is between about 20 and 40 weight percent. In another embodiment the loading is about 40 weight percent.

[0043] The supports upon which the metal species is to be deposited may be of any size and composition that is capable of being dispersed/suspended in the solution during the removal of heat to precipitate the metal species. The maximum size depends on several parameters including agitation of the suspension, density of the supports, specific gravity of the solution, and the rate at which heat is removed from the system. In general, the supports are electrically conductive and are useful for supporting electrocatalytic compounds in fuel cells. Such electrically conductive supports are typically inorganic, for example, carbon supports. However, the electrically conductive supports may comprise an organic material such as an electrically conductive polymer (see, e.g., in U.S. Pat. Appln. 2002/0132040 A1). Carbon supports may be predominantly amorphous or graphitic and they may be prepared commercially, or specifically treated to increase their graphitic nature (e.g., heat treated at a high temperature in vacuum or in an inert gas atmosphere) thereby increasing corrosion resistance. Carbon black support particles may have a Brunauer, Emmett and Teller (BET) surface area up to about 2000 m²/g. It has been reported that satisfactory results are achieved using carbon black support particles having a high mesoporous area, e.g., greater than about 75 m²/g (see, e.g.,

Catalysis for Low Temperature Fuel Cells Part 1: The Cathode Challenges, T.R. Ralph and M.P. Hogarth, *Platinum Metals Rev.*, 2002, 46, (1), p. 3-14).

Experimental results to date indicate that a surface area of about 500 m²/g is preferred.

[0044] In another embodiment the supports have pre-deposited material thereon. For example, when the final composition of the deposits on the carbon supports is a platinum alloy, it may be advantageous to use a carbon supported platinum powder. Such powders are commercially available from companies such as Johnson Matthey, Inc., of New Jersey and E-Tek Div. of De-Nora, N.A., Inc., of Sommerset, New Jersey and may be selected to have a particular loading of platinum. The amount of platinum loading is selected in order to achieve the desired stoichiometry of the supported metal alloy. Typically, the loading of platinum is between about 5 and about 60 weight percent. In one embodiment the loading of platinum is between about 15 and 45 weight percent. The size (*i.e.*, the maximum cross-sectional length) of the platinum deposits is typically less than about 20 nm. In other embodiments of the invention the size of the platinum deposits is less than about 10 nm, 5 nm, or 2 nm, and may be smaller. In another embodiment of the invention the size of the platinum deposits is between about 2 and about 3 nm. Experimental results to date indicate that a desirable supported platinum powder may be further characterized by having a platinum surface area of between about 150 and about 170 m²/g (determined by CO adsorption), a combined carbon and platinum surface area between about 350 and about 400 m²/g (determined by N₂ adsorption), and an average support size that is between about 100 and 300 nm.

[0045] The solution and supports are mixed according to any appropriate method to form the dispersion/suspension. Exemplary methods include magnetic stirring, insertion of a stirring structure such as a rotor, shaking, sonication, or a combination of the foregoing methods. Provided that the supports can be adequately mixed with the solution, the relative amounts of supports and solution may vary over a wide range. For example, when preparing carbon supported metal electrocatalysts using an aqueous suspension comprising dissolved inorganic metal-containing compounds, the carbon supports typically comprise between about 1 and about 30 weight percent of the suspension. In other embodiments the carbon supports comprise between about 1 and about 15 weight percent of the suspension, between about 1 and about 10 weight percent of the suspension, between about 3 and about 8 weight percent of the suspension, between about 5 and about 7 weight percent of the suspension, and about 6 weight percent of the suspension. The relative amounts of supports and solution may also be described in terms of volume ratios. In one embodiment the dispersion/suspension has a volume ratio of support

particles to solution of at least about 1:10. Specifying a minimum volume ratio indicates that the volume of support particles may be increased relative to the volume of solution. In other embodiments the volume ratio is at least about 1:8, 1:5, and 1:2.

[0046] In one embodiment of the present invention the solution and supports are mixed using sonication at a power and for a duration sufficient to form a dispersion/suspension in which the pores of the supports are impregnated with the solution and/or the supports are uniformly distributed throughout the solution. If the suspension is not uniformly mixed (*i.e.*, the supports are not uniformly impregnated with the solution and/or the supports are not uniformly distributed throughout the solution), the deposits formed on the supports will typically be non-uniform (*e.g.*, the loading of the metal species may vary among the supports, the size of the deposits may vary significantly on a support and/or among the supports, and/or the composition of the deposits may vary among the supports). Although a uniform mixture is generally preferred, there may be circumstances in which a non-uniform mixture is desirable.

[0047] Typically the uniformity of the suspension is maintained throughout the removal of heat from the suspension. This uniformity may be maintained by continuing the mixing of the suspension as it is being cooled. In one embodiment, however, the uniformity is maintained by the viscosity of the dispersion/suspension. The actual viscosity needed to suspend the particles uniformly depends in large part on the amount of supports in the dispersion/suspension and the size of the supports. To a lesser degree, the necessary viscosity depends on the density of the supports and the specific gravity of the solution. In general, it is typically sufficient to prevent substantial settling of the supports as the heat is being removed from the suspension to precipitate the deposits, and in one embodiment until the dispersion/suspension is frozen. The degree of settling, if any, may be determined, for example, by examining portions of the frozen suspension. Typically, substantial settling would be considered to have occurred if the concentrations of supports in any two portions vary by more than about $\pm 10\%$. When preparing a carbon support metal electrocatalyst powder in accordance with one embodiment of the invention the viscosity is typically sufficient to prevent settling for at least about 4 minutes. In other embodiments the viscosity prevents settling for at least about 10 minutes, about 30 minutes, about 1 hour, and even up to about 2 days. In another embodiment the viscosity of the dispersion/suspension is at least about 5,000 mPa·s.

[0048] Heat is removed from the dispersion/suspension so that at least a part of the solute portion separates from the solvent portion and deposits (*e.g.*,

precipitates) the metal species onto the supports and/or onto any pre-existing deposits (e.g., pre-deposited platinum or deposits formed by precipitation of incompatible solutes). If the concentration of supports in the suspension is sufficient (e.g., within the ranges set forth above) and enough heat is removed, nearly all of the metal species to be deposited is separated from the solvent portion to form deposits (e.g., precipitates) comprising the metal species on the supports. In one embodiment the heat is removed to freeze the dispersion/suspension and form a composite comprising the supports with deposits comprising the metal species on the supports within a matrix of the solvent portion in a solid state. If the concentration of the solute portion in the solution exceeds the ability of the supports to accommodate deposits of the metal species, some of the solute portion may crystallize within the matrix. If this occurs, such crystals are not considered to be a supported powder.

[0049] In one embodiment of the present invention the deposits of metal species are precursors of a metal alloy and the size of the metal species deposits is controlled such that the eventually formed metal alloy deposits are of size suitable for use as a fuel cell electrocatalyst (e.g., 20 nm, 10 nm, 5 nm, 3 nm (30 Å), 2 nm (20 Å) or smaller). As set forth above, this is accomplished in part by maintaining a well impregnated and uniformly distributed suspension throughout the removal of heat from the system. Additionally, this is accomplished by rapidly removing heat from the dispersion/suspension as the compound or compounds are depositing on supports.

[0050] The rapid heat removal may be accomplished by cooling the suspension from a temperature of at least about 20 °C to a temperature below the freezing point of the solvent (e.g., at a rate of least about 20 °C/minute). In one embodiment the suspension is cooled at a rate of at least about 50 °C/minute. In another embodiment the suspension is cooled at a rate between about 50 and 100 °C/minute. Typically, such cooling rates freeze the suspension from a temperature such as room temperature (about 20 °C) or higher (e.g., about 100 °C) within a freezing period of not more than about 10, 5, or 3 minutes.

[0051] The heat may be removed from the dispersion/suspension by any appropriate method. For example, a container containing a volume of dispersion/suspension may be placed within a refrigeration unit such as freeze-dryer, a volume of dispersion/suspension may be contacted with a cooled surface (e.g., a plate or container), a volume of dispersion/suspension in a container may be immersed in, or otherwise contacted with, a cryogenic liquid. Advantageously, the same container may also be used during the formation of the dispersion and/or during the separation of solvent from deposited supports. In one embodiment a

cover is placed over an opening of the container. Although the cover may completely prevent the escape of any solid matter from the container, in one embodiment the cover allows for a gas to exit the container and substantially prevents the supports from exiting the container. An example of such a cover includes a stretchable film (e.g., PARAFILM) having holes that are, for example, less than about 500 μm in size (maximum length across the hole).

[0052] In one embodiment the dispersion/suspension is cooled at a rate of at least about 20 $^{\circ}\text{C}/\text{minute}$ by immersing a container containing the dispersion/suspension in a volume of cryogenic liquid within a cryogen container sized and shaped so that at least about 50, 60, 70, 80, or 90 percent of the surface of the dispersion/suspension container is contacted with the cryogenic liquid. The cryogenic liquid is typically at a temperature that is at least about 20 $^{\circ}\text{C}$ below the freezing point of the solvent. Examples of suitable cryogenic liquids typically include liquid nitrogen, liquid helium, liquid argon, but even less costly media may be utilized. For example an ice water/hydrous calcium chloride mixture can reach temperatures down to about -55 $^{\circ}\text{C}$, an acetone/dry ice mixture that can reach temperatures down to about -78 $^{\circ}\text{C}$, and a diethyl ether/dry ice mixture that can reach temperatures down to about -100 $^{\circ}\text{C}$.

[0053] The container may be made of nearly any type of material. Generally, the selected material does not require special handling procedures, can withstand repeated uses without structural failure (e.g., resistant to thermal shock), does not contribute impurities to the suspension (e.g., resistant to chemical attack), and is thermally conductive. For example, plastic vials made from high density polyethylene may be used.

[0054] The supports having the deposits thereon may be separated from the solvent portion by any appropriate method such as filtration, evaporation (e.g., by spray-drying), sublimation (e.g., freeze-drying), or a combination thereof. The evaporation or sublimation rate may be enhanced by adding heat (e.g., raising the temperature of the solvent) and/or decreasing the atmospheric pressure to which the solvent is exposed.

[0055] In one embodiment a frozen suspension is freeze-dried to remove the solvent portion from the frozen suspension. The freeze-drying may be carried out in any appropriate apparatus such as a LABONCO FREEZE DRY SYSTEM (Model 79480). Intuitively, one of skill in the art would typically maintain the temperature of the frozen suspension below the melting point of the solvent (*i.e.*, the solvent is removed by sublimation) in order to prevent agglomeration of the supports. The process of the present invention may be carried out under such conditions. Surprisingly, however, it is not critical that solvent portion not be allowed to melt.

Specifically, it has been discovered that a free-flowing, and non-agglomerated powder may be prepared even if the solvent is allowed to melt provided that the pressure within the freeze-dryer is maintained at a level that the evaporation rate of the liquid solvent is faster than the melting rate (e.g., below about 0.2 millibar, 0.000197 atm, or 20 Pa). Thus, there is typically not enough solvent in the liquid state to result in agglomeration of the supports. Advantageously, this can be used to decrease the time needed to remove the solvent portion. Removing the solvent portion forms a free-flowing and non-agglomerated supported powder that comprises the supports and deposits of the metal species on the supports.

[0056] To accomplish the conversion from precursor to metal, the powder is typically heated in a reducing atmosphere (e.g., an atmosphere containing hydrogen and/or an inert gas such as argon) at a temperature sufficient to decompose the precursor. The temperature reached during the thermal treatment is typically at least as high as the decomposition temperature(s) for the precursor compound(s) and not be so high as to result in degradation of the supports and agglomeration of the supports. Typically the temperature is between about 60 °C and about 1100 °C. Organometallic compounds tend to decompose at lower temperatures (e.g., 200 °C and lower), whereas inorganic metal-containing compounds typically decompose at higher temperatures (e.g., between about 200 and 1000 °C). Typically, the temperature does not exceed about 1000 °C, which is adequate for forming/alloying most metals.

[0057] The duration of the heat treatment is typically at least sufficient to substantially convert the precursor deposits to the desired state. In general, the temperature and time are inversely related (*i.e.*, conversion is accomplished in a shorter period of time at higher temperatures and vice versa). At the temperatures typical for converting the inorganic metal-containing compounds to a metal alloy set forth above, the duration of the heat treatment is typically at least about 30 minutes. In one embodiment, the duration is between about 2 and about 7 hours.

[0058] Referring to Figure. 1, a carbon supported metal alloy electrocatalyst powder particle **1** produced in accordance with the method of the present invention comprises a carbon support **2** and deposits **3** of the metal alloy on the support. A particle and a powder comprising said particles may have a loading that is up to about 90 weight percent. However, when a supported metal powder is used as a fuel cell electrocatalyst, the loading is typically between about 5 and about 60 weight percent, and in one embodiment between about 20 and about 40 weight percent. Increasing the loading to greater than about 60 weight percent does not typically result in an increase in the activity. Without being held to a particular theory, it is believed the excess loading covers a portion of the deposited metal and the covered

portion cannot catalyze the desired electrochemical reaction. On the other hand, the activity of the supported metal electrocatalyst typically decreases significantly if the loading is below about 5 weight percent.

[0059] This freeze-dry method may be used to produce supported metal alloy powders that are heavily loaded with nanoparticle deposits of a metal alloy that comprises one or more non-noble metals, wherein the deposits have a relatively narrow size distribution. In one embodiment the supported non-noble metal-containing metal alloy powder has a metal loading of at least about 20 weight percent of the powder, an average deposit size that is no greater than about 10 nm, and a deposit size distribution in which at least about 70 percent of the deposits are within about 50 and 150 percent of the average deposit size. In other embodiments the metal loading is between about 20 and about 60 weight percent, or between about 20 and about 40 weight percent. In other embodiments the average size of the metal alloy deposits is no greater than about 5 nm (50 Å), no greater than 3 nm (30 Å), or no greater than about 2 nm (20 Å). In another embodiment the average size of the metal alloy deposits is between about 5 nm and about 10 nm. In another embodiment the size distribution of the deposits is such that at least about 80 percent of the deposits are within about 75 and 125 percent of the average deposit size.

[0060] The freeze-dry method of preparing supported electrocatalyst powders allows for superior control of the stoichiometry of the deposits because the suspension is preferably kept within a single container, the solution is not physically separated from the supports (e.g., by filtration), and freezing results in substantially all of the solute precipitating on the supports. Additionally, the deposits tend to be isolated, small, and uniformly dispersed over the surface of the supports and thereby increasing the overall electrocatalytic activity. Still further, because filtering is not necessary, extremely fine particles are not lost and the supported metal powders produced by the present method tend to have a greater surface area and activity. Also, the act of depositing the metal species on the supports is fast. For example, immersing a container of the suspension in a cryogenic liquid can solidify the suspension in about three to four minutes.

Unsupported Catalyst or Alloys in Electrode/fuel Cell Applications

[0061] It is to be noted that, in another embodiment of the present invention, the metal substance (e.g., catalyst or alloy) may be unsupported; that is, it may be employed in the absence of a support particle. More specifically, it is to be noted that in another embodiment of the present invention a metal catalyst or alloy,

comprising platinum and copper, may be directly deposited (e.g., sputtered) onto, for example, (i) a surface of one or both of the electrodes (e.g., the anode, the cathode or both), and/or (ii) one or both surfaces of a polyelectrolyte membrane, and/or (iii) some other surface, such as a backing for the membrane (e.g., carbon paper).

[0062] In this regard it is to be further noted that each component (e.g., metal) of the catalyst or alloy may be deposited separately, each for example as a separate layer on the surface of the electrode, membrane, etc. Alternatively, two or more components may be deposited at the same time. Additionally, in the case of an alloy, the alloy may be formed and then deposited, or the components thereof may be deposited and then the alloy subsequently formed thereon.

[0063] Deposition of the component(s) may be achieved using means known in the art, including for example known sputtering techniques (see, e.g., PCT Application No. WO 99/16137). Generally speaking, however, in one approach sputter-deposition is achieved by creating, within a vacuum chamber in an inert atmosphere, a voltage differential between a target component material and the surface onto which the target component is to be deposited, in order to dislodge particles from the target component material which are then attached to the surface of, for example, an electrode or electrolyte membrane, thus forming a coating of the target component thereon. In one embodiment, the components are deposited on a polymeric electrolyte membrane, including for example (i) a copolymer membrane of tetrafluoroethylene and perfluoropolyether sulfonic acid (such as the membrane material sold under the trademark NAFION), (ii) a perfluorinated sulfonic acid polymer (such as the membrane material sold under the trademark ACIPLEX), (iii) polyethylene sulfonic acid polymers, (iv) polyketone sulfonic acids, (v) polybenzimidazole doped with phosphoric acid, (vi) sulfonated polyether sulfones, and (vii) other polyhydrocarbon-based sulfonic acid polymers.

[0064] It is to be noted that the specific amount of each metal or component of the catalyst or alloy may be controlled independently, in order to tailor the composition to a given application. In some embodiments, however, the amount of each deposited component may be less than about 5 mg/cm² of surface area (e.g., electrode surface area, membrane surface area, etc.), less than about 1 mg/cm², less than about 0.5 mg/cm², less than about 0.1 mg/cm², or even less than about 0.05 mg/cm². Alternatively, in some embodiments the amount of the deposited component, or alloy, may range from about 0.5 mg/cm² to less than about 5 mg/cm², or from about 0.1 mg/cm² to less than about 1 mg/cm².

[0065] It is to be further noted that the specific amount of each component, and/or the conditions under which the component is deposited, may be controlled in order to control the resulting thickness of the component, or alloy, layer on the

surface of the electrode, electrolyte membrane, etc. For example, as determined by means known in the art (e.g., scanning electron microscopy or Rutherford back scattering spectrophotometric method), the deposited layer may have a thickness ranging from several angstroms (e.g., about 2, 4, 6, 8, 10 or more) to several tens of angstroms (e.g., about 20, 40, 60, 80, 100 or more), up to several hundred angstroms (e.g., about 200, 300, 400, 500 or more). Additionally, after all of the components have been deposited, and/or alloyed (or, alternatively, after the alloy has been deposited), the layer of the multi-component metal substance of the present invention may have a thickness ranging from several tens of angstroms (e.g., about 20, 40, 60, 80, 100 or more), up to several hundred angstroms (e.g., about 200, 400, 600, 800, 1000, 1500 or more). Thus, in different embodiments the thickness may be, for example, between about 10 and about 500 angstroms, between about 20 and about 200 angstroms, and between about 40 and about 100 angstroms.

[0066] It is to be still further noted that in embodiments wherein a catalyst or alloy (or the components thereof) are deposited as a thin film on the surface of, for example, an electrode or electrolyte membrane, the composition of the deposited catalyst or alloy may be as previously described herein. Additionally, in other embodiments, the composition of the deposited catalyst or alloy may be other than as previously described. For example, with respect to an embodiment of an unsupported catalyst or alloy, the concentration of copper may be 50 percent or less.

Incorporation of an Electrocatalyst Composition in a Fuel Cell

[0067] The alloy compositions of the present invention are particularly suited for use in proton exchange membrane fuel cells. As shown in Figures 2 and 3, a fuel cell, generally indicated **20**, comprises a fuel electrode (anode) **22** and an air electrode, oxidizer electrode (cathode) **23**. In between the electrodes **22** and **23**, a proton exchange membrane **21** serves as an electrolyte and it is usually a strongly acidic ion exchange membrane such as a perfluorosulphonic acid-based membrane. Preferably, the proton exchange membrane **21**, the anode **22**, and the cathode **23** are integrated into one body to minimize contact resistance between the electrodes and the proton exchange membrane. Current collectors **24** and **25** engage the anode and the cathode, respectively. A fuel chamber **28** and an air chamber **29** contain the respective reactants and are sealed by sealants **26** and **27**, respectively.

[0068] In general, electricity is generated by hydrogen-containing fuel combustion (i.e., the hydrogen-containing fuel and oxygen react to form water,

carbon dioxide and electricity). This is accomplished in the above-described fuel cell by introducing the hydrogen-containing fuel **F** into the fuel chamber **28**, while oxygen **O** (preferably air) is introduced into the air chamber **29**, whereby an electric current can be immediately transferred between the current collectors **24** and **25** through an outer circuit (not shown). Ideally, the hydrogen-containing fuel is oxidized at the anode **22** to produce hydrogen ions, electrons, and possibly carbon dioxide gas. The hydrogen ions migrate through the strongly acidic proton exchange membrane **21** and react with oxygen and electrons transferred through the outer circuit to the cathode **23** to form water. If the hydrogen-containing fuel **F** is methanol, it is preferably introduced as a dilute acidic solution to enhance the chemical reaction, thereby increasing power output (e.g., a 0.5 M methanol/0.5 M sulfuric acid solution).

[0069] To prevent the loss of ionic conduction in the proton exchange membranes, they typically remain hydrated during operation of the fuel cell. As a result, the material of the proton exchange membrane is typically selected to be resistant to dehydration at temperatures up to between about 100 and about 120 °C. Proton exchange membranes usually have reduction and oxidation stability, resistance to acid and hydrolysis, sufficiently low electrical resistivity (e.g., <10 $\Omega\cdot\text{cm}$), and low hydrogen or oxygen permeation. Additionally, proton exchange membranes are usually hydrophilic. This ensures proton conduction (by reversed diffusion of water to the anode), and prevents the membrane from drying out thereby reducing the electrical conductivity. For the sake of convenience, the layer thickness of the membranes is typically between 50 and 200 μm . In general, the foregoing properties are achieved with materials that have no aliphatic hydrogen-carbon bonds, which, for example, are achieved by replacing hydrogen with fluorine or by the presence of aromatic structures; the proton conduction results from the incorporation of sulfonic acid groups (high acid strength). Suitable proton-conducting membranes also include perfluorinated sulfonated polymers such as NAFION and its derivatives produced by E.I. du Pont de Nemours & Co., Wilmington, Delaware. NAFION is based on a copolymer made from tetrafluoroethylene and perfluorovinylether, and is provided with sulfonic groups working as ion-exchanging groups. Other suitable proton exchange membranes are produced with monomers such as perfluorinated compounds (e.g., octafluorocyclobutane and perfluorobenzene), or even monomers with C—H bonds that do not form any aliphatic H atoms in a plasma polymer, which could constitute attack sites for oxidative breakdown.

[0070] The electrodes of the present invention comprise the electrocatalyst compositions of the present invention and an electrode substrate upon which the electrocatalyst is deposited. In one embodiment the electrocatalyst alloy is directly

deposited on the electrode substrate. In another embodiment the electrocatalyst alloy is supported on electrically conductive supports and the supported electrocatalyst is deposited on the electrode substrate. The electrode may also comprise a proton conductive material that is in contact with the electrocatalyst. The proton conductive material may facilitate contact between the electrolyte and the electrocatalyst, and may thus enhance fuel cell performance. Preferably, the electrode is designed to increase cell efficiency by enhancing contact between the reactant (i.e., fuel or oxygen), the electrolyte and the electrocatalyst. In particular, porous or gas diffusion electrodes are typically used since they allow the fuel/oxidizer to enter the electrode from the face of the electrode exposed to the reactant gas stream (back face), and the electrolyte to penetrate through the face of the electrode exposed to the electrolyte (front face), and reaction products, particularly water, to diffuse out of the electrode.

[0071] Preferably, the proton exchange membrane, electrodes, and electrocatalyst materials are in contact with each other. This is typically accomplished by depositing the electrocatalyst either on the electrode, or on the proton exchange membrane, and then placing the electrode and membrane in contact. The alloy electrocatalysts of this invention can be deposited on either the electrode or the membrane by a variety of methods, including plasma deposition, powder application (the powder may also be in the form of a slurry, a paste, or an ink), chemical plating, and sputtering. Plasma deposition generally entails depositing a thin layer (e.g., between 3 and 50 μm , preferably between 5 and 20 μm) of an electrocatalyst composition on the membrane using low-pressure plasma. By way of example, an organic platinum compound such as trimethylcyclopentadienylplatinum is gaseous between 10^{-4} and 10 mbar and can be excited using radio-frequency, microwaves, or an electron cyclotron resonance transmitter to deposit platinum on the membrane. According to another procedure, electrocatalyst powder is distributed onto the proton exchange membrane surface and integrated at an elevated temperature under pressure. If, however, the amount of electrocatalyst particles exceeds about 2 mg/cm^2 the inclusion of a binder such as polytetrafluoroethylene is common. Further, the electrocatalyst may be plated onto dispersed small support particles (e.g., the size is typically between 20 and 200 \AA , and more preferably between about 20 and 100 \AA). This increases the electrocatalyst surface area, which in turn increases the number of reaction sites leading to improved cell efficiency. In one such chemical plating process, for example, a powdery carrier material such as conductive carbon black is contacted with an aqueous solution or aqueous suspension (slurry) of compounds of metallic components constituting the alloy to permit adsorption or impregnation of the

metallic compounds or their ions on or in the carrier. Then, while the slurry is stirred at high speed, a dilute solution of suitable fixing agent such as ammonia, hydrazine, formic acid, or formalin is slowly added dropwise to disperse and deposit the metallic components on the carrier as insoluble compounds or partly reduced fine metal particles.

[0072] The loading, or surface concentration, of an electrocatalyst on the membrane or electrode is based in part on the desired power output and cost for a particular fuel cell. In general, power output increases with increasing concentration; however, there is a level beyond which performance is not improved. Likewise, the cost of a fuel cell increases with increasing concentration. Thus, the surface concentration of electrocatalyst is selected to meet the application requirements. For example, a fuel cell designed to meet the requirements of a demanding application such as an extraterrestrial vehicle will usually have a surface concentration of electrocatalyst sufficient to maximize the fuel cell power output. For less demanding applications, economic considerations dictate that the desired power output be attained with as little electrocatalyst as possible. Typically, the loading of electrocatalyst is between about 0.01 and about 6 mg/cm². Experimental results to date indicate that in some embodiments the electrocatalyst loading is preferably less than about 1 mg/cm², and more preferably between about 0.1 and 1 mg/cm².

[0073] To promote contact between the collector, electrode, electrocatalyst, and membrane, the layers are usually compressed at high temperature. The housings of the individual fuel cells are configured in such a way that a good gas supply is ensured, and at the same time the product water can be discharged properly. Typically, several fuel cells are joined to form stacks, so that the total power output is increased to economically feasible levels.

[0074] In general, the electrocatalyst compositions and fuel cell electrodes of the present invention may be used to electrocatalyze any fuel containing hydrogen (e.g., hydrogen and reformed-hydrogen fuels). Also, hydrocarbon-based fuels may be used including saturated hydrocarbons such as methane (natural gas), ethane, propane and butane; garbage off-gas; oxygenated hydrocarbons such as methanol and ethanol; and fossil fuels such as gasoline and kerosene; and mixtures thereof.

[0075] To achieve the full ion-conducting property of proton exchange membranes, in some embodiments suitable acids (gases or liquids) are typically added to the fuel. For example, SO₂, SO₃, sulfuric acid, trifluoromethanesulfonic acid or the fluoride thereof, also strongly acidic carboxylic acids such as

trifluoroacetic acid, and volatile phosphoric acid compounds may be used ("Ber. Bunsenges. Phys. Chem.", Volume 98 (1994), pages 631 to 635).

Fuel Cell Uses

[0076] As set forth above, the alloy compositions of the present invention are useful as electrocatalysts in fuel cells that generate electrical energy to perform useful work. For example, the alloy compositions may be used in fuel cells which are in electrical utility power generation facilities; uninterrupted power supply devices; extraterrestrial vehicles; transportation equipment such as heavy trucks, automobiles, and motorcycles (see, Fuji et al., U.S. Pat. No. 6,048,633; Shinkai et al., U.S. Pat. No. 6,187,468; Fuji et al., U.S. Pat. No. 6,225,011; and Tanaka et al., U.S. Pat. No. 6,294,280); residential power generation systems; mobile communications equipment such as wireless telephones, pagers, and satellite phones (see, Prat et al., U.S. Pat. No. 6,127,058 and Kelley et al., U.S. Pat. No. 6,268,077); mobile electronic devices such as laptop computers, personal data assistants, audio recording and/or playback devices, digital cameras, digital video cameras, and electronic game playing devices; military and aerospace equipment such as global positioning satellite devices; and robots.

Example 1 - Forming Electrocatalytic Alloys on Individually Addressable Electrodes

[0077] The electrocatalyst alloy compositions set forth in Tables A and B, infra, were prepared using the combinatorial techniques disclosed in Warren et al., U.S. Pat. No. 6,187,164; Wu et al., U.S. Pat. No. 6,045,671; Strasser, P., Gorer, S. and Devenney, M., *Combinatorial Electrochemical Techniques For The Discovery of New Fuel-Cell Cathode Materials*, Nayayanan, S.R., Gottesfeld, S. and Zawodzinski, T., eds., Direct Methanol Fuel Cells, Proceedings of the Electrochemical Society, New Jersey, 2001, p. 191; and Strasser, P., Gorer, S. and Devenney, M., *Combinatorial Electrochemical Strategies For The Discovery of New Fuel-Cell Electrode Materials*, Proceedings of the International Symposium on Fuel Cells for Vehicles, 41st Battery Symposium, The Electrochemical Society of Japan, Nagoya 2000, p. 153. For example, an array of independent electrodes (with areas of between about 1 and 3 mm²) may be fabricated on inert substrates (e.g., glass, quartz, sapphire alumina, plastics, and thermally treated silicon). The individual electrodes were located substantially in the center of the substrate, and were connected to contact pads around the periphery of the substrate with wires. The electrodes, associated wires, and contact pads were fabricated from a conducting

material (e.g., titanium, gold, silver, platinum, copper or other commonly used electrode materials).

[0078] Specifically, the alloy compositions set forth in Tables A and B were prepared using a photolithography/RF magnetron sputtering technique (GHz range) to deposit thin-film alloys on arrays of 64 individually addressable electrodes. A quartz insulating substrate was provided and photolithographic techniques were used to design and fabricate the electrode patterns on it. By applying a predetermined amount of photoresist to the substrate, photolyzing preselected regions of the photoresist, removing those regions that have been photolyzed (e.g., by using an appropriate developer), depositing a layer of titanium about 500 nm thick using RF magnetron sputtering over the entire surface and removing predetermined regions of the deposited titanium (e.g. by dissolving the underlying photoresist), intricate patterns of individually addressable electrodes were fabricated on the substrate.

[0079] Referring to Figure 4, the fabricated array **40** consisted of 64 individually addressable electrodes **41** (about 1.7 mm in diameter) arranged in an 8 x 8 square that were insulated from each other (by adequate spacing) and from the substrate **44** (fabricated on an insulating substrate), and whose interconnects **42** and contact pads **43** were insulated from the electrochemical testing solution (by the hardened photoresist or other suitable insulating material).

[0080] After the initial array fabrication and prior to depositing the electrocatalyst alloys for screening, a patterned insulating layer covering the wires and an inner portion of the peripheral contact pads was deposited, but leaving the electrodes and the outer portion of the peripheral contact pads exposed (preferably approximately half of the contact pad is covered with this insulating layer). Because of the insulating layer, it is possible to connect a lead (e.g., a pogo pin or an alligator clip) to the outer portion of a given contact pad and address its associated electrode while the array is immersed in solution, without having to worry about reactions that can occur on the wires or peripheral contact pads. The insulating layer was a hardened photoresist, but any other suitable material known to be insulating in nature could have been used (e.g., glass silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide, or titanium dioxide).

[0081] Following the creation of the titanium-coated array, a steel mask having 64 holes (1.7 mm in diameter) was pressed onto the substrate to prevent deposition of sputtered material onto the insulating resist layer. The deposition of the electrocatalyst alloys was also accomplished using RF magnetron sputtering and a two shutter masking system as described by Wu et al. which enable the deposition of material onto 1 or more electrodes at a time. Each individual thin-film

electrocatalyst alloy was created by a super lattice deposition method. For example, when preparing a binary alloy electrocatalyst composition, metals M1 and M2 are to be deposited and alloyed onto one electrode. First, a metal M1 sputter target is selected and a thin film of M1 having a defined thickness is deposited on the electrode. This initial thickness is typically from about 3 to about 12 Å. After this, metal M2 is selected as the sputter target and a layer of M2 is deposited onto the layer of M1. The thickness of M2 layer is also from about 3 to about 12 Å. The thicknesses of the deposited layers are in the range of the diffusion length of the metal atoms (e.g., about 10 to about 30 Å) which allows in-situ alloying of the metals to form a M1-M2 alloy film. As a result of the two deposition steps, an alloy thin-film (6 - 25 Å thickness) of the desired stoichiometry is created. This concludes one deposition cycle. In order to achieve the desired total thickness of a cathode electrocatalyst material, deposition cycles are repeated as necessary which results in the creation of a super lattice structure of a defined total thickness (typically about 700 Å). Although the number, thickness (stoichiometry) and order of application of the individual metal layers may be determined manually, it is desirable to utilize a computer program to design an output file which contains the information necessary to control the operation of the sputtering device during the preparation of a particular library wafer (i.e., array). One such computer program is the LIBRARY STUDIO software available from Symyx Technologies, Inc. of Santa Clara, California and described in European Patent No. 1080435 B1. The compositions of several as sputtered alloy compositions were analyzed using x-ray fluorescence (XRF) to confirm that they were consistent with desired compositions (chemical compositions determined using x-ray fluorescence are within about 5% of the actual composition).

[0082] Arrays were prepared to evaluate the specific alloy compositions set forth in Tables A and B below. On each array one electrode consisted essentially of platinum and it served as an internal standard for the screening of the alloys on that array.

Table A

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt atomic %	Cu atomic %
133379	6	-0.48	-0.59	1.62	60	40
133802	8	-1.17	-1.43	1.58	60	40
132991	27	-0.93	-1.23	1.55	50	50
134165	55	-1.41	-1.71	1.45	60	40

126556	6	-0.15	-0.18	1.44	60	40
134165	64	-1.37	-1.67	1.42	60	40
133802	35	-1.04	-1.47	1.41	44	56
130758	8	-1.24	-1.51	1.39	60	40
132971	27	-1.00	-1.32	1.34	50	50
132991	6	-0.79	-0.96	1.32	60	40
130758	35	-1.15	-1.62	1.29	44	56
133379	27	-0.37	-0.49	1.24	50	50
126556	27	-0.13	-0.17	1.22	50	50
133802	40	-0.89	-0.97	1.21	80	20
133802	51	-0.89	-1.04	1.20	67	33
132971	6	-0.87	-1.06	1.17	60	40
133815	35	-0.71	-1.00	1.08	45	55
133803	40	-0.81	-0.88	1.07	80	20
133815	51	-0.70	-0.81	1.06	67	33
133352	35	-0.81	-1.14	1.03	44	56
130758	51	-0.92	-1.07	1.03	67	33
133803	35	-0.78	-1.09	1.02	44	56
133815	8	-0.67	-0.82	1.02	60	40
133352	51	-0.79	-0.92	1.01	67	33
133803	51	-0.76	-0.88	1.00	67	33
130758	40	-0.88	-0.95	0.99	80	20
133803	8	-0.74	-0.90	0.98	60	40
133815	40	-0.64	-0.69	0.97	80	20
133352	8	-0.73	-0.89	0.93	60	40
133352	40	-0.72	-0.78	0.92	80	20
133802	3	-0.47	-1.01	0.64	22	78
126556	30	-0.05	-0.12	0.50	20	80
133352	3	-0.37	-0.79	0.47	22	78
133379	30	-0.12	-0.27	0.40	20	80
132991	30	-0.23	-0.52	0.38	20	80
132971	30	-0.17	-0.38	0.22	20	80
133815	3	-0.10	-0.21	0.15	22	78
133803	3	-0.10	-0.20	0.13	22	78
134165	63	-0.05	-0.11	0.05	20	80
130758	3	0.01	0.01	-0.01	22	78

* Each array contains an internal Pt reference electrode. Thus, each array is relative to the internal reference present on that array.

Table B

Array Number	Electrode Number	End Current Density (Absolute Activity) mA/cm ²	End Current Density per Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt atomic %	Cu atomic %
136300*	1	-4.05	-7.30	6.46	29	71
136300*	2	-3.83	-6.52	6.11	32	68
136300*	3	-3.20	-5.13	5.11	35	65
136300*	4	-2.02	-3.04	3.23	39	61

136299	1	-1.16	-2.10	1.35	29	71
136299	2	-1.14	-1.95	1.33	32	68
136300*	7	-0.79	-0.95	1.26	62	38
136300*	5	-0.74	-1.04	1.19	45	55
136300*	6	-0.74	-0.97	1.19	52	48
137656	49	-0.58	-0.71	1.17	60	40
136299	3	-0.98	-1.57	1.14	35	65
137564	49	-0.62	-0.76	1.10	60	40
136299	7	-0.93	-1.12	1.08	62	38
136299	4	-0.92	-1.38	1.07	39	61
136299	5	-0.90	-1.26	1.04	45	55
136299	6	-0.90	-1.17	1.04	52	48
137674	49	-0.24	-0.30	0.80	60	40

* Array 136300 was heated to about 400 °C for about 12 hours in vacuum prior to being screened in attempts to mimic powder synthesis.

Example 2 - Screening Alloys for Electrocatalytic Activity

[0083] The alloy compositions set forth in Tables A and B that were synthesized on arrays according to the method set forth in Example 1 were screened for electrochemical reduction of molecular oxygen to water to determine relative electrocatalytic activity against the internal and/or external platinum standard.

[0084] In general, the array wafers were assembled into an electrochemical screening cell and a screening device established an electrical contact between the 64 electrode electrocatalysts (working electrodes) and a 64-channel multi channel potentiostat used for the screening. Specifically, each wafer array was placed into a screening device such that all 64 spots are facing upward and a tube cell body that was generally annular and having an inner diameter of about 2 inches (5 cm) was pressed onto the upward facing wafer surface. The diameter of this tubular cell was such that the portion of the wafer with the square electrode array formed the base of a cylindrical volume while the contact pads were outside the cylindrical volume. A liquid ionic solution (i.e., 0.5 M H₂SO₄ aqueous electrolyte) was poured into this cylindrical volume and a common counter electrode (i.e., platinum gauze) and a common reference electrode (e.g., mercury/mercury sulfate reference electrode (MMS)) were placed into the electrolyte solution to close the electrical circuit.

[0085] A rotator shaft with blades was also placed into the electrolyte to provide forced convection-diffusion conditions during the screening. The rotation rate was typically between about 300 to about 400 rpm. Depending on the screening experiment either argon or pure oxygen was bubbled through the electrolyte during the measurements. Argon served to remove O₂ gas in the

electrolyte to simulate O₂-free conditions used for the initial conditioning of the electrocatalysts. The introduction of pure oxygen served to saturate the electrolyte with oxygen for the oxygen reduction reaction. During the screening, the electrolyte was maintained at 60 °C and the rotation rate was constant. Three groups of tests were performed to screen the activity of the electrocatalysts. The electrolyte was purged with argon for about 20 minutes prior to the electrochemical measurements. The first group of tests comprised cyclic voltammetric measurements while purging the electrolyte with argon. Specifically, the first group of tests comprised:

- a. a potential sweep from open circuit potential (OCP) to about +0.3 V to about -0.63 V and back to about +0.3 V at a rate of about 20 mV/s;
- b. seventy-five consecutive potential sweeps from OCP to about +0.3 V to about -0.7 V and back to about +0.3 V at a rate of about 200 mV/s; and
- c. a potential sweep from OCP to about +0.3 V to about -0.63 V and back to about +0.3 V at a rate of about 20 mV/s.

The shape of the cyclic voltammetric (CV) profile of the internal Pt standard catalyst as obtained in test c) was compared to an external standard CV profile obtained from a Pt thin-film electrode that had been pretreated until a stable CV was obtained. If test c resulted in a similar cyclic voltammogram, the first group of experiments was considered completed. If the shape of the cyclic voltammogram of test c did not result in the expected standard Pt CV behavior, tests b and c were repeated until the Pt standard catalyst showed the desired standard voltammetric profile. This way, it was ensured that the Pt standard catalyst showed a stable and well-defined oxygen reduction activity in subsequent experiments. The electrolyte was then purged with oxygen for approximately 30 minutes. The following second group of tests were performed while continuing to purge with oxygen:

- a. measuring the open circuit potential (OCP) for a minute; then, the potential was stepped to ?0.4 V, held for a minute, and was then swept up to about +0.4 V at a rate of about 10 mV/s;
- b. measuring the OCP for a minute; then applying a potential step from OCP to about +0.1 V while measuring the current for about 5 minutes; and
- c. measuring the OCP for a minute; then applying a potential step from OCP to about +0.2 V while monitoring the current for about 5 minutes.

The third group of tests comprised a repeat of the second group of tests after about one hour from completion of the second group of tests. The electrolyte was continually stirred and purged with oxygen during the waiting period. All the

foregoing test voltages are with reference to a mercury/mercury sulfate (MMS) electrode. Additionally, an external platinum standard comprising an array of 64 platinum electrodes in which the oxygen reduction activity of the 64 platinum electrodes averaged -0.35 mA/cm^2 at $+0.1 \text{ V}$ vs. a mercury/mercury sulfate electrode was used to monitor the tests to ensure the accuracy of the oxygen reduction evaluation.

[0086] The specific alloy compositions set forth in Tables A and B were prepared and screened in accordance with the above-described methods and the results are set forth therein. The screening results in Tables A and B are for the third test group steady state currents at $+0.1 \text{ V}$ MMS. The current value reported (End Current Density) is the result of averaging the last three current values of the chronoamperometric test normalized for geometric surface area.

Example 3 - Synthesis of Supported Electrocatalyst Alloys

[0087] The synthesis of Pt-Cu alloys (see, Table C, Target Catalyst Comp., *infra*) on carbon support particles was attempted according to different process conditions in order to evaluate the performance of the alloys while in a state that is typically used in fuel cell. To do so, the alloy component precursors were deposited or precipitated on supported platinum powder (i.e., platinum nanoparticles supported on carbon black particles). Platinum supported on carbon black is commercially available from companies such as Johnson Matthey, Inc., of New Jersey and E-Tek Div. of De-Nora, N.A., Inc., of Somerset, New Jersey. Such supported platinum powder is available with a wide range of platinum loading. The supported platinum powder used in this example had a nominal platinum loading of about 40 or 20 percent by weight, a platinum surface area of between about 150 and about 170 m^2/g (determined by CO adsorption), a combined carbon and platinum surface area between about 350 and about 400 m^2/g (determined by N_2 adsorption), and an average particle size of less than about 0.5 μm (determined by sizing screen).

[0088] Electrocatalyst alloys corresponding to the target composition described in Table C were formed on carbon support particles using a freeze-drying precipitation method. The freeze-drying method comprised forming a precursor solution comprising the desired metal atoms in the desired concentrations. Each of the supported alloys was prepared in an analogous manner with variations in the amounts of metal-containing compounds. For example, the target $\text{Pt}_{25}\text{Cu}_{75}$ alloy composition (HFC 344) was prepared by dissolving about 0.143 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a vial containing about 5 ml of H_2O . This solution was introduced into a HDPE vial

containing the 0.200 g of supported platinum powder that had a nominal platinum loading of about 19.2 percent by weight resulting in a black suspension. The suspension was homogenized by immersing a probe of a BRANSON SONIFIER 150 into the vial and sonicating the mixture for about 90 seconds at a power level of 3. The vial containing the homogenized suspension was then immersed in a liquid nitrogen bath for about 3 minutes to solidify the suspension. The solid suspension was then freeze-dried for about 24 hours using a LABONCO FREEZE DRY SYSTEM (Model 79480) to remove the solvent. The tray and the collection coil of the freeze dryer were maintained at about 26 °C and about -49 °C, respectively, while evacuating the system (the pressure was maintained at about 0.15 mbar). During the final 2.5 hrs of the freeze-drying procedure, the shelve heater was set to 40 °C. After completing the procedure, the vial contained a powder comprising the supported platinum powder, and the copper precursor deposited thereon.

[0089] The recovered precursor powders were then subjected to a heat treatment to reduce the precursor to the metallic state, and to alloy the copper and the platinum on the carbon black particles. The heat treatment comprised heating the powder in a quartz flow furnace with an atmosphere comprising about 6% H₂ and 94% Ar using a temperature profile of room temperature to about 40 °C at a rate of about 5 °C/min; holding at about 40 °C for 2 hours; increasing the temperature to about 200 °C at a rate of 5 °C/min; holding at about 200 °C for two hours; increasing the temperature at a rate of about 5 °C/min to a maximum temperature of about 500, 600, 700 or 900 °C; holding at the maximum for a duration of about two or seven hours (indicated in Table C); and cooling down to room temperature.

[0090] In order to determine the actual composition of the supported electrocatalyst alloys, certain differently prepared alloys (e.g., by composition variation or by heat treatment variation) were subjected to EDS (Electron Dispersive Spectroscopy) elemental analysis. The sample powders were compressed into 6 mm diameter pellets with a thickness of about 1 mm. The target alloy composition and actual composition for the prepared supported electrocatalyst alloys are also set forth in Table C.

Table C

Powder Name	Target Catalyst Comp.	Max Alloying Temp for a duration (°C/hrs)	Actual Catalyst Comp.	Target Pt Loading (wt%)	Measured Pt Loading (wt%)	Log Pt Mass Activity at +0.15 V MMS	Pt Mass Activity at +0.15 V MMS (mA/mg Pt)	Relative performance at +0.15 V MMS	Catalyst Mass Activity at +0.15 V MMS (mA/mg)	Lattice parameter (Å) uncorrected	Approx. particle size (Å)
HFC 010	Pt	-	Pt	37.8	37.8	2.11	128.82	1.00	48.7	3.942	19
HFC 287	Pt ₃₅ Cu ₆₅	700 / 7	-	17.2	-	-	-	3.51	77.73	3.763	23
HFC 290	Pt ₃₅ Cu ₆₅	900 / 2	-	17.2	-	-	-	2.38	52.84	3.763	33
HFC 344	Pt ₂₅ Cu ₇₅	700 / 7	-	16.2	-	-	-	3.60	75.20	3.714	26
HFC 345	Pt ₃₀ Cu ₇₀	700 / 7	-	16.7	-	-	-	2.66	57.33	3.763	26
HFC 346	Pt ₄₀ Cu ₆₀	700 / 7	-	17.5	-	-	-	2.28	51.30	3.795	25
HFC 347	Pt ₄₅ Cu ₅₅	700 / 7	-	17.8	-	-	-	2.27	52.03	3.790	23
HFC 360	Pt ₁₆ Cu ₈₄	700 / 7	-	14.3	-	-	-	3.18	58.62	3.705	34
HFC 361	Pt ₂₀ Cu ₈₀	700 / 7	-	15.2	-	-	-	2.98	58.41	3.718	28
HFC 362	Pt ₂₅ Cu ₇₅	700 / 7	-	16.0	-	-	-	3.63	74.80	3.723	27
HFC 363	Pt ₃₀ Cu ₇₀	700 / 7	Pt ₃₅ Cu ₆₅	16.6	15.5	2.86	718.12	5.57	111.31	3.738	25
HFC 364	Pt ₃₅ Cu ₆₅	700 / 7	-	17.0	-	-	-	3.34	73.17	3.765	23
HFC 365	Pt ₄₀ Cu ₆₀	700 / 7	-	17.4	-	-	-	3.42	76.64	3.783	22
HFC 367	Pt ₁₆ Cu ₈₄	600 / 7	-	14.3	-	-	-	3.77	69.52	3.702	31
HFC 368	Pt ₂₀ Cu ₈₀	600 / 7	-	15.2	-	-	-	3.56	69.63	3.708	28
HFC 369	Pt ₂₅ Cu ₇₅	600 / 7	Pt ₂₉ Cu ₇₁	16.0	14.8	2.83	683.03	5.30	101.09	3.722	26

HFC 370	Pt ₃₀ Cu ₇₀	600 / 7	-	16.6	-	-	-	-	4.36	93.24	3.738	24
HFC 371	Pt ₃₅ Cu ₆₅	600 / 7	-	17.0	-	-	-	-	4.52	98.94	3.763	23
HFC 372	Pt ₄₀ Cu ₆₀	600 / 7	-	17.4	-	-	-	-	4.11	92.14	3.784	22
HFC 374	Pt ₂₅ Cu ₇₅	600 / 7	-	14.5	-	-	-	-	4.18	77.99	3.783	17
HFC 375	Pt ₃₀ Cu ₇₀	600 / 7	-	15.0	-	-	-	-	3.83	73.94	3.785	17
HFC 376	Pt ₂₅ Cu ₇₅	600 / 7	-	25.0	-	-	-	-	1.92	61.97	3.756	27
HFC 377	Pt ₃₀ Cu ₇₀	600 / 7	-	26.4	-	-	-	-	1.36	46.25	3.732	29
HFC 378	Pt ₂₅ Cu ₇₅	500 / 7	-	14.5	-	-	-	-	2.29	42.85	3.793	16
HFC 379	Pt ₃₀ Cu ₇₀	500 / 7	-	15.0	-	-	-	-	1.88	36.41	3.811	15
HFC 380	Pt ₂₅ Cu ₇₅	500 / 7	-	25.0	-	-	-	-	0.88	28.31	3.743	33
HFC 381	Pt ₃₀ Cu ₇₀	500 / 7	-	26.4	-	-	-	-	1.46	49.50	3.765	29
HFC 382	Pt ₂₅ Cu ₇₅	600 / 7	Pt ₃₀ Cu ₇₀	16.0	15.1	2.86	721.46	-	5.60	108.94	3.729	23
HFC 383	Pt _{27.5} Cu _{72.5}	600 / 7	Pt ₃₂ Cu ₆₈	16.5	15.1	2.89	780.83	-	6.06	117.91	3.730	23
HFC 384	Pt ₃₀ Cu ₇₀	600 / 7	-	16.6	-	-	-	-	4.08	87.18	3.744	24
HFC 385	Pt _{32.5} Cu _{67.5}	600 / 7	-	16.8	-	-	-	-	3.53	76.45	3.760	21
HFC 386	Pt ₃₅ Cu ₆₅	600 / 7	-	17.0	-	-	-	-	3.61	79.07	3.770	24
HFC 387	Pt ₂₅ Cu ₇₅	700 / 7	-	16.0	-	-	-	-	4.24	87.37	3.732	24
HFC 388	Pt _{27.5} Cu _{72.5}	700 / 7	-	16.5	-	-	-	-	3.48	74.00	3.734	26
HFC 389	Pt ₃₀ Cu ₇₀	700 / 7	-	16.6	-	-	-	-	4.45	95.17	3.742	27
HFC 390	Pt _{32.5} Cu _{67.5}	700 / 7	-	16.8	-	-	-	-	4.07	88.17	3.764	23
HFC 391	Pt ₃₅ Cu ₆₅	700 / 7	-	17.0	-	-	-	-	3.75	82.22	3.776	25

Example 4 - Evaluation of Electrocatalytic Activity of Supported Electrocatalysts

[0091] The supported alloy electrocatalysts set forth in Table C and formed according to Example 3 were subjected to electrochemical measurements to evaluate their activities. For the evaluation, the supported alloy electrocatalysts were applied to a rotating disk electrode (RDE) as is commonly used in the art (see, Rotating disk electrode measurements on the CO tolerance of a high-surface area Pt/Vulcan carbon fuel cell electrocatalyst, Schmidt et al., Journal of the Electrochemical Society (1999), 146(4), 1296-1304; and Characterization of high-surface-area electrocatalysts using a rotating disk electrode configuration, Schmidt et al., Journal of the Electrochemical Society (1998), 145(7), 2354-2358). Rotating disk electrodes are a relatively fast and simple screening tool for evaluating supported electrocatalysts with respect to their intrinsic electrolytic activity for oxygen reduction (e.g., the cathodic reaction of a fuel cell).

[0092] The rotating disk electrodes were prepared by depositing an aqueous-based ink that comprises the support electrocatalyst and a NAFION solution on a glassy carbon disk. The concentration of electrocatalyst powder in the NAFION solution was about 1 mg/mL. The NAFION solution comprised the perfluorinated ion-exchange resin, lower aliphatic alcohols and water, wherein the concentration of resin is about 5 percent by weight. The NAFION solution is commercially available from the ALDRICH catalog as product number 27,470-4. The glassy carbon electrodes were 5 mm in diameter and were polished to a mirror finish. Glassy carbon electrodes are commercially available, for example, from Pine Instrument Company of Grove City, Pennsylvania. For each electrode, an aliquot of 10 μ L electrocatalyst suspension was added to the carbon substrate and allowed to dry at a temperature between about 60 and 70 °C. The resulting layer of NAFION and electrocatalyst was less than about 0.2 μ m thick. This method produced slightly different platinum loadings for each electrode made with a particular suspension, but the variation was determined to be less than about 10 percent by weight.

[0093] After being dried, each rotating disk electrode was immersed into an electrochemical cell comprising an aqueous 0.5 M H₂SO₄ electrolyte solution maintained at room temperature. Before performing any measurements, the electrochemical cell was purged of oxygen by bubbling argon through the electrolyte

for about 20 minutes. All measurements were taken while rotating the electrode at about 2000 rpm, and the measured current densities were normalized either to the glassy carbon substrate area or to the platinum loading on the electrode. Two groups of tests were performed to screen the activity of the supported electrocatalysts. The first group of tests comprised cyclic voltammetric measurements while purging the electrolyte with argon. Specifically, the first group comprised:

- a. two consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 50 mV/s;
- b. two hundred consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 200 mV/s; and
- c. two consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 50 mV/s.

The second test comprised purging with oxygen for about 15 minutes followed by a potential sweep test for oxygen reduction while continuing to purge the electrolyte with oxygen. Specifically, potential sweeps from about -0.45 V to +0.35 V were performed at a rate of about 5 mV/s to evaluate the initial activity of the electrocatalyst as a function of potential and to create a geometric current density plot. The electrocatalysts were evaluated by comparing the diffusion corrected activity at 0.15 V. All the foregoing test voltages are with reference to a mercury/mercury sulfate electrode. Also, it is to be noted that the oxygen reduction measurements for a glassy carbon RDE without an electrocatalyst did not show any appreciable activity within the potential window.

[0094] The above-described supported electrocatalyst alloy compositions were evaluated in accordance with the above-described method and the results are set forth in Table C. The carbon supported alloy target compositions $\text{Pt}_{16}\text{Cu}_{84}$, $\text{Pt}_{20}\text{Cu}_{80}$, $\text{Pt}_{25}\text{Cu}_{75}$, $\text{Pt}_{27.5}\text{Cu}_{72.5}$, $\text{Pt}_{30}\text{Cu}_{70}$, $\text{Pt}_{32.5}\text{Cu}_{67.5}$, $\text{Pt}_{35}\text{Cu}_{65}$, $\text{Pt}_{40}\text{Cu}_{60}$, and $\text{Pt}_{45}\text{Cu}_{55}$ exhibited oxygen reduction activities greater than that of carbon supported platinum. The results of the evaluation also indicate, among other things, that it may take numerous iterations to develop a set of parameters for producing the target alloy composition. Also evidenced by the data, is that activity can be adjusted by changes in the processing conditions.

[0095] Further, without being held to a particular theory, it is presently believed that differences in activity for similar alloy compositions may be due to several factors such as alloy homogeneity (e.g., an alloy, as defined below, may have regions in which the constituent atoms show a presence or lack of order, i.e., regions of solid solution within an ordered lattice, or some such superstructure), changes in the lattice parameter due to changes in the average size of component atoms, changes in particle size, and changes in crystallographic structure/symmetry. The ramifications of synthesis, structure and symmetry changes are often difficult to predict. For example, while it may be expected that within the Pt-Cu system the two metals will be fully miscible, the possibility exists that ordering may occur between the two metals at the atomic level. The possibility exists that as the relative ratio of copper to platinum changes, a solid solution may crystallize (e.g., $Pt_{1-x}Cu_x$), and out of this solid solution an ordered phase may gradually crystallize (e.g., $Pt_{50}Cu_{50}$) only to return to a solid solution (disordered alloy) and again back to an ordered phase (e.g., $Pt_{25}Cu_{75}$).

[0096] As discussed above, symmetry changes (e.g., those associated with the changes from a cubic face centered structure to another structure type) may result in significant changes in the X-ray diffraction pattern. These changes may also be accompanied by more subtle changes in lattice parameters that may be indicative of the resulting changes in the size of the respective metal constituents. For example, the 12-coordinate metallic radii of platinum and copper are 1.387 Å and 1.278 Å, respectively. As one metal is substituted for another, the average metal radius and, consequently, the observed lattice parameter may be expected to shrink or expand accordingly. Thus, the average radius may be used as an indicator of lattice changes as a function of stoichiometry, or alternatively, as an indicator of stoichiometry based on observed lattice parameters. It should be noted, however, that while average radii may be useful as a general rule, experimental results should be expected to conform only in a general manner because local ordering, significant size disparity between atoms, significant changes in symmetry, and/or other factors may produce values that are inconsistent with expectations. Occasionally, the use of alternative metallic radii may be useful. One such alternative radius concept approximates metal radii using known crystallographically ordered Pt-based alloys such as PtCu (cubic symmetry is maintained) instead of pure metals. In this case,

the same close-packed geometric arguments are relevant with the exception that the lattice parameter of the ordered metal alloy is used in conjunction with the accepted 12-coordinate metallic radius of platinum. According to the alternative radius concept, it is believed that the effective radius of copper is about 1.284 Å.

[0097] An interpretation of XRD analyses for the foregoing supported alloys is set forth below. Because the interpretation of XRD analyses can be subjective, the following conclusions are not intended to be limiting. The powders listed in Table C were analyzed to determine both the lattice parameter, assuming a face-centered cubic lattice, and the observed particle size (i.e., the size of the metal-containing deposits on the supports). The peak positions were corrected using silicon powder (SRM 640c). The average particle sizes of the alloy deposits, not of any copper or copper-rich impurity phases, were determined using the Scherrer formula. The term "particle size" as used herein with respect to the size of metal deposits on the supports shall be interpreted as the average particle size. The supported platinum powder used to prepare all the catalysts except HFC 374-381 (i.e., the standard supported platinum powder) had a particle size of 19 Å. The HFC 374-381 catalysts were prepared with two alternative supported platinum powders. The HFC 374, 375, 378, and 379 were prepared with a first alternative supported platinum powder that consisted of carbon supports as described above with platinum metal deposits having a particle size that is smaller than 19 Å. Specifically, the first alternative powder has a loading of between about 16 and about 18 weight percent, and a particle size of about 12 and about 19 Å. The second alternative powder has a platinum loading of between about 30 and about 35 weight percent.

[0098] All the catalysts displayed XRD patterns of a face-centered cubic material, however, certain materials displayed slight indications of ordering (see description of the different catalysts below). In general, the observed lattice parameters agreed with what was expected for the particular target alloy compositions. However, in some circumstances the lattice parameters were larger than what was anticipated, and based on the XRD profile (e.g., the presence of additional peaks or peak shape irregularities) it is believed that this discrepancy is due, at least in part, to the presence of incompletely reacted, or alloyed, copper or copper-rich impurities. For example, referring to Figure 5 the general background pattern is due to the presence of carbon, peaks A, B, and C are that of a platinum-

copper alloy deposits and peaks X, Y, and Z are that of copper and/or copper-rich impurity deposits. The narrower aspect of the copper/copper-rich impurity peaks is due to the fact that the impurity deposits are larger in size than the platinum-copper alloy deposits. Because of the presence of copper or copper-rich impurities, the amount of platinum in the alloy deposits is actually greater than the target composition and this results in a larger observed lattice parameter. Additionally, the results generally indicate that as the copper content in the target stoichiometry increases there is greater tendency to have more unreacted, or unalloyed, copper or copper-rich impurities and the electrochemical performance tends to decrease.

[0099] The observed lattice parameters of the $\text{Pt}_{16}\text{Cu}_{84}$ catalysts (HFC 360 and 367) are consistent with the amount of copper impurities (i.e., although the global stoichiometry of the supported electrocatalyst may be $\text{Pt}_{16}\text{Cu}_{84}$, the presence of the copper impurities results in an empirical stoichiometry of $\text{Pt}_{16+x}\text{Cu}_{84-x}$ and a concomitant increase in the observed lattice parameter). Specifically, the lattice parameters of HFC 360 and 367 are about 3.705 Å and about 3.702 Å, respectively, and the relative performance of HFC 367 is about 18.5% greater than HFC 360. Additionally, the differences in heat treatments resulted in differences in particle sizes; the observed lattice parameters of the $\text{Pt}_{20}\text{Cu}_{80}$ catalysts (HFC 361 and 368) are similarly consistent with the amount of copper impurities.

[0100] The observed lattice parameters of the $\text{Pt}_{25}\text{Cu}_{75}$ catalysts (HFC 344, 362, 369, 374, 376, 378, 380, 382 and 387) varied according to the starting supported platinum powder that was used. In general, the alloys prepared from the alternative supported platinum powders (HFC 374, 376, 378, and 380) had larger lattice parameters, and more crystalline copper or copper-rich impurities. Accordingly, the electrochemical performance of these materials suffered compared to the materials prepared using the standard supported platinum powder. The observed lattice parameters for alloys prepared using the standard supported platinum powder are consistent with each other and the alloy stoichiometry as measured by EDS. At this time, it is not known exactly why the catalysts produced by the alternative powders were less reacted than those produced with the standard powder. It is believed that more complete alloying may be achieved through routine experimentation to determine the optimum values of one or more process parameters such as alloying temperature and/or duration. Upon determining the

optimum values, it is possible that the alternative supported platinum powders, especially the powder having platinum particles of a size less than the standard powder, will result alloy particles that yield greater electrochemical performance due, at least in part, to the smaller particle size.

[0101] The observed lattice parameters of the $\text{Pt}_{27.5}\text{Cu}_{72.5}$ catalysts (HFC383 and 388) are generally consistent with the stoichiometry as measured by EDS. The differences in particle sizes are also consistent with the synthesis temperatures and seem to contribute to electrochemical performance (i.e., lower synthesis temperatures tend to produce smaller particles that tend to result in greater electrochemical activity than larger particles of the same composition).

[0102] The observed lattice parameters of the $\text{Pt}_{30}\text{Cu}_{70}$ catalysts (HFC 345, 363, 370, 375, 377, 379, 381, 384, and 389) vary according to the starting material used. In general, the alloys prepared from the alternative supported platinum powders (HFC 375, 377, 379, and 381) had larger lattice parameters and more copper or copper-rich impurities. Accordingly, the electrochemical performance of these materials suffered compared to the materials prepared using the standard supported platinum powder. The observed lattice parameters for alloys prepared using the standard supported platinum powder are consistent with each other and the alloy stoichiometry as measured by EDS. Among the alloys prepared using the standard supported platinum powder, those with more copper or copper-rich impurities tend to under-perform electrochemically.

[0103] The observed lattice parameters of the $\text{Pt}_{32.5}\text{Cu}_{67.5}$ catalysts (HFC 385 and 390) are larger than expected. Specifically, the observed parameters for HFC 854 and 390 are 3.760 and 3.764, respectively, whereas the calculated lattice parameter is 3.725. The observed particle sizes are consistent with the synthesis temperature (i.e., higher synthesis temperatures tend to produce larger the particles).

[0104] The observed lattice parameters of the $\text{Pt}_{35}\text{Cu}_{65}$ catalysts (HFC 287, 290, 364, 371, 386, 391) are generally consistent with the observed copper or copper-rich impurities. The particle sizes increased with increasing synthesis temperatures. The observed electrochemical activity of the 900 °C material was less than that for the 700 °C material. The electrochemical activity of the 700 °C materials is considered to be consistent with stoichiometry. It is believed that the relatively low

electrochemical performance of HFC 386 is due to incomplete alloying at the relatively low temperature of 600 °C.

[0105] The Pt₄₀Cu₆₀ catalysts (HFC 346, 365, and 372) seem to be consistent with the general rule that increasing synthesis temperature tend to result in increasing particle size and decreasing electrochemical activity. The lattice parameter of HFC 346 is largest because it had the largest amount of copper and/or copper-rich impurities. This is believed to be a reason why it had a lower activity than the HFC 365 catalyst, which was also prepared at 700 °C.

[0106] The observed lattice parameter of the Pt₄₅Cu₅₅ catalyst (HFC 347) is larger than expected for the stoichiometry because of copper and/or copper-rich impurities as previously discussed. The observed particle size is consistent with the synthesis temperature.

[0107] In view of the foregoing, for a particular electrocatalyst composition a determination of the optimum conditions is preferred to produce the highest activity for that particular composition. In fact, for certain electrocatalyst compositions, different structural characteristics may define what exactly is described as a "good" electrocatalyst. These characteristics may include differences in the composition (as viewed by lattice parameter), crystallinity, crystallographic ordering and/or particle size. These characteristics are not necessarily predictable and may depend on a complex interplay between starting materials, synthesis method, synthesis temperature and composition. For example, the starting materials used to synthesize the alloy may play a role in the activity of the synthesized alloy. Specifically, using something other than a metal nitrate salt solution to supply the metal atoms may result in different activities. Additionally, alternative Pt sources may be employed. Freeze-drying and heat treatment parameters such as atmosphere, time, temperature, etc. may also need to be optimized. This optimization may be compositionally dependent. Additionally, this optimization may involve balancing competing phenomena. For example, increasing the heat treatment temperature is generally known to improve the reduction of a metal salt to a metal, which typically increases activity; however, it also tends to increase the size of the electrocatalyst alloy particle and decrease surface area, which decreases electrocatalytic activity.

Definitions

[0108] Activity is defined as the maximum sustainable, or steady state, current (Amps) obtained from the electrocatalyst, when fabricated into an electrode, at a given electric potential (Volts). Additionally, because of differences in the geometric area of electrodes, when comparing different electrocatalysts, activity is often expressed in terms of current density (A/cm^2). An alloy is a mixture comprising two or more metals. An alloy may be described as a solid solution in which the solute and solvent atoms (the term solvent is applied to the metal that is in excess) are arranged at random, much in the same way as a liquid solution may be described. If some solute atoms replace some of those of the solvent in the structure of the latter, the solid solution may be defined as a substitutional solid solution. Alternatively, an interstitial solid solution is formed if a smaller atom occupies the interstices between the larger atoms. Combinations of the two types are also possible. Furthermore, in certain solid solutions, some level of regular arrangement may occur under the appropriate conditions resulting in a partial ordering that may be described as a superstructure. These solid solutions may have characteristics that may be distinguishable through characterization techniques such as XRD. Significant changes in XRD may be apparent due to changes in symmetry. Although the global arrangement of the metal atoms may be similar in the case of a solid solution and an ordered alloy, the relationship between the specific locations of the metal A and metal B atoms is now ordered, not random, resulting in different diffraction patterns. Further, a homogeneous alloy is a single compound comprising the constituent metals. A heterogeneous alloy comprises an intimate mixture of crystals of individual metals and/or metallic compounds (see, Structural Inorganic Chemistry, A.F. Wells, Oxford University Press, 5th Edition, 1995, chapter 29). An alloy, as defined herein, is also meant to include materials that may comprise elements that are generally considered to be non-metallic. For example, some alloys of the present invention may comprise oxygen in atomic, molecular, and/or metallic oxide form. Additionally, some alloys of the present invention may comprise carbon in atomic, molecular, and/or metal carbide form. If present, the amount of oxygen and/or carbon in the alloy is typically at what is generally considered to be a low level (e.g., less than about 5 weight percent) and is typically considered to be an impurity (e.g., less than

about 2, 1, 0.5, 0.1 atomic percent), however higher concentrations are also possible (e.g., up to about 10 weight percent).

[0109] It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should therefore be determined not with reference to the above description alone, but should be determined with reference to the claims and the full scope of equivalents to which such claims are entitled.

[0110] When introducing elements of the present invention or an embodiment thereof, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0111] The recitation of numerical ranges by endpoints includes all numbers subsumed within that range. For example, a range described as being between 1 and 5 includes 1, 1.6, 2, 2.8, 3, 3.2, 4, 4.75, and 5.

CLAIMS

What is claimed is:

1. A supported metal alloy powder, the supported metal alloy powder comprising metal alloy deposits on electrically conductive supports, wherein the metal alloy deposits comprise platinum and copper, a concentration of copper that is greater than 50 atomic percent, and an average size that is no greater than about 30 Å.
2. The supported metal alloy powder of claim 1 wherein the concentration of copper is no greater than about 90 atomic percent.
3. The supported metal alloy powder of claim 1 having a concentration of platinum that is no less than about 10 atomic percent.
4. The supported metal alloy powder of claim 1 wherein the concentration of copper is between about 60 and about 80 atomic percent.
5. The supported metal alloy powder of claim 1 having a concentration of platinum that is between about 20 and about 40 atomic percent.
6. The supported metal alloy powder of claim 1 wherein the concentration of copper is between about 65 and about 75 atomic percent.
7. The supported metal alloy powder of claim 1 having a concentration of platinum that is between about 25 and about 35 atomic percent.
8. The supported metal alloy powder as in any one of claims 1-7 wherein the metal alloy deposits consist essentially of platinum and copper.

9. The supported metal alloy powder of claim 1 wherein electrically conductive supports are selected from the group consisting of inorganic supports and organic supports.

10. The supported metal alloy powder of claim 1 wherein the electrically conductive supports are selected from the group consisting of carbon supports and electrically conductive polymer supports.

11. The supported metal alloy powder of claim 1 having a loading of metal alloy deposits on the electrically conductive supports of at least about 20 weight percent.

12. The supported metal alloy powder of claim 1 having a loading of metal alloy deposits on the electrically conductive supports that is between about 20 and about 60 weight percent of the electrically conductive supports.

13. The supported metal alloy powder of claim 1 having a loading of metal alloy deposits on the electrically conductive supports that is between about 20 and about 40 weight percent of the electrically conductive supports.

14. The supported metal alloy powder of claim 1 wherein the average size of the metal alloy deposits is no greater than about 20 Å.

15. The supported metal alloy powder of claim 1 wherein the average size of the metal alloy deposits is between about 10 and about 20 Å.

16. The supported metal alloy powder of claim 1 having a deposit size distribution wherein at least about 70 percent of the metal alloy deposits are between about 50 and about 150 percent of the average size of the metal alloy deposits.

17. The supported metal alloy powder of claim 1 having a deposit size distribution wherein at least about 80 percent of the metal alloy deposits are between about 75 and about 125 percent of the average size of the metal alloy deposits.

18. A supported metal alloy powder, the supported metal alloy powder comprising wherein the metal alloy deposits comprise platinum and copper, a lattice parameter that is no more than 3.777 Å, and an average size that is no greater than about 30 Å.

19. The supported metal alloy powder of claim 18 wherein the lattice parameter is between about 3.674 and about 3.765 Å.

20. The supported metal alloy powder of claim 18 wherein the lattice parameter is between about 3.689 and about 3.750 Å.

21. The supported metal alloy powder of claim 18 wherein the lattice parameter is between about 3.704 and about 3.745 Å.

22. A fuel cell electrode, the fuel cell electrode comprising a supported metal alloy powder as in any one of claims 1-21 and an electrode substrate upon which the supported electrocatalyst powder is deposited.

23. A fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and a catalyst for the catalytic oxidation of a hydrogen-containing fuel or the catalytic reduction of oxygen, the catalyst comprising an alloy comprising platinum and copper, wherein the concentration of copper in the alloy is greater than 50 atomic percent.

24. The fuel cell of claim 23 wherein the concentration of copper is no greater than about 90 atomic percent.

25. The fuel cell of claim 23 wherein the concentration of copper is between about 55 and about 85 atomic percent.

26. The fuel cell of claim 23 wherein the concentration of copper is between about 60 and about 80 atomic percent.

27. The fuel cell of claim 23 wherein the concentration of copper is between about 65 and about 75 atomic percent.

28. The fuel cell as in any one of claims 23-27 wherein the catalyst consists essentially of platinum and copper.

29. The fuel cell of claim 23 wherein the catalyst is the supported metal alloy powder as in any one of claims 1-21.

30. The fuel cell of claim 23 wherein the catalyst is on the surface of the proton exchange membrane and in contact with the anode.

31. The fuel cell of claim 23 wherein the catalyst is on the surface of the anode and in contact with the proton exchange membrane.

32. The fuel cell of claim 23 wherein the catalyst is on the surface of the proton exchange membrane and in contact with the cathode.

33. The fuel cell of claim 23 wherein the catalyst is on the surface of the cathode and in contact with the proton exchange membrane.

34. A method for the electrochemical conversion of a hydrogen-containing fuel and oxygen to reaction products and electricity in a fuel cell as in any one of claims 23-33, and an electrically conductive external circuit connecting the anode and cathode, the method comprising contacting the hydrogen-containing fuel or the oxygen and the catalyst to catalytically oxidize the hydrogen-containing fuel or catalytically reduce the oxygen.

35. The method of claim 34 wherein the hydrogen-containing fuel consists essentially of hydrogen.

36. The method of claim 34 wherein the hydrogen-containing fuel is a hydrocarbon-based fuel selected from the group consisting of saturated hydrocarbons, garbage off-gas, oxygenated hydrocarbons, fossil fuels, and mixtures thereof.

37. The method of claim 34 wherein the hydrogen-containing fuel is methanol.

38. An unsupported catalyst layer on a surface of an electrolyte membrane or an electrode, said unsupported catalyst layer comprising platinum and copper, wherein the concentration of copper is greater than 50 atomic percent.

ABSTRACT

A metal alloy composition for a fuel cell electrocatalyst, the metal alloy contains platinum and copper and the concentration of copper comprises more than 50 atomic percent of the electrocatalyst composition.

FIG. 1

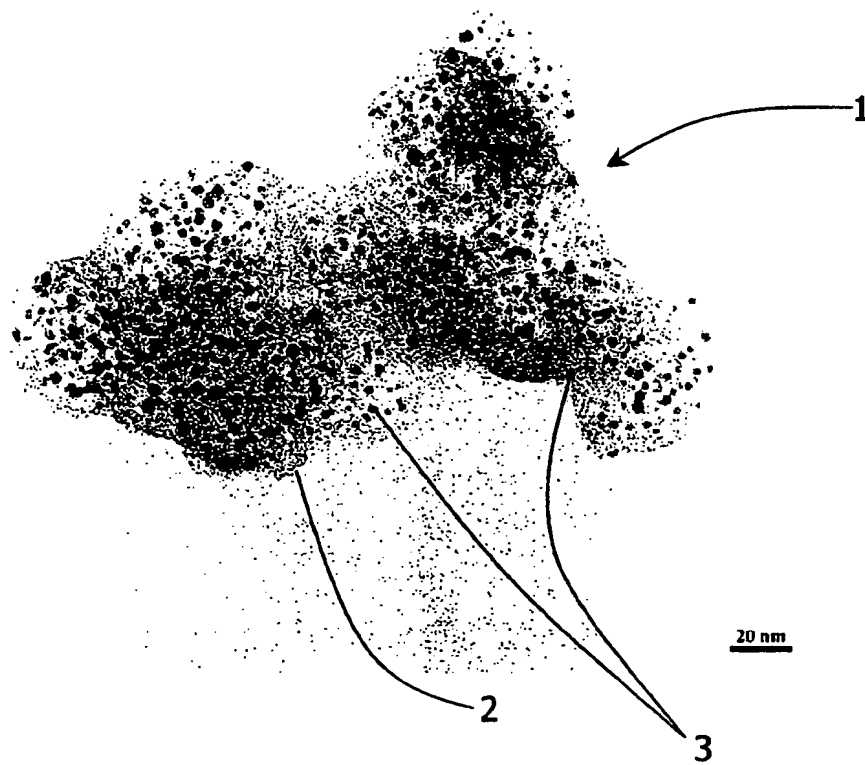


FIG. 2

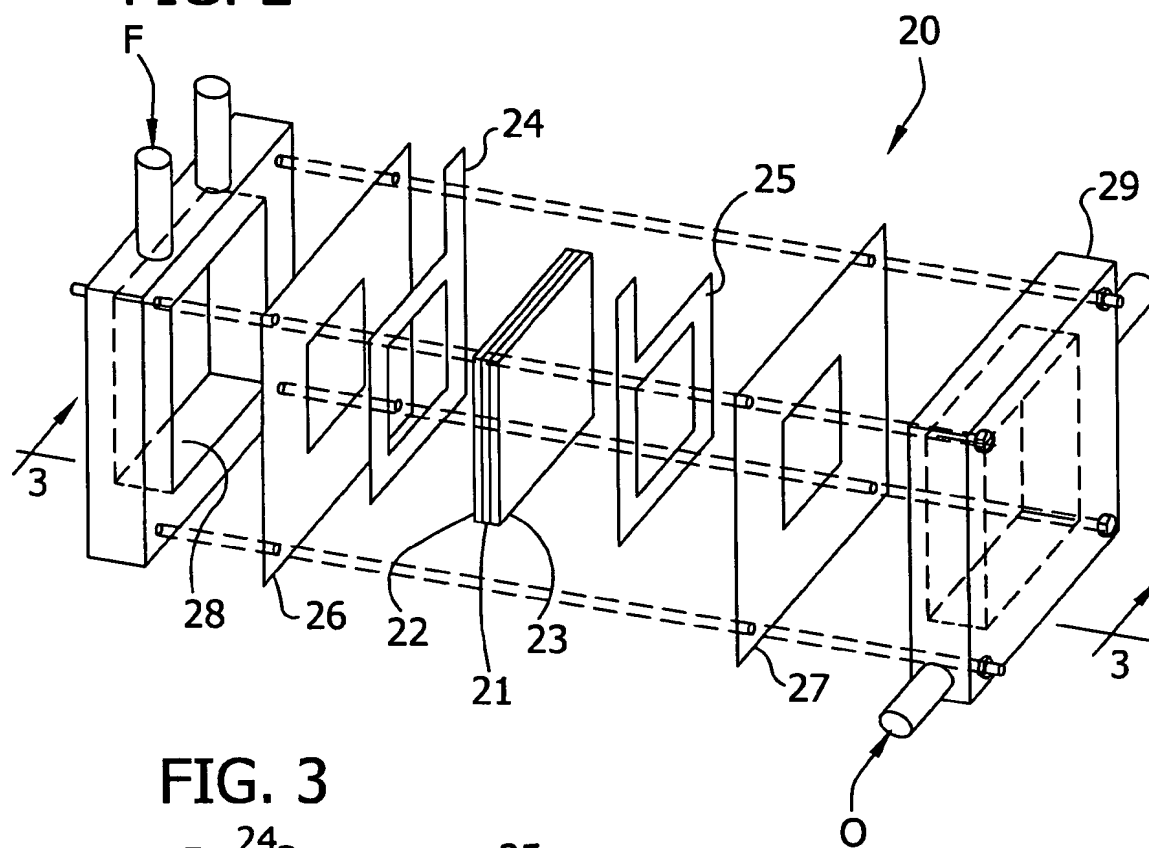


FIG. 3

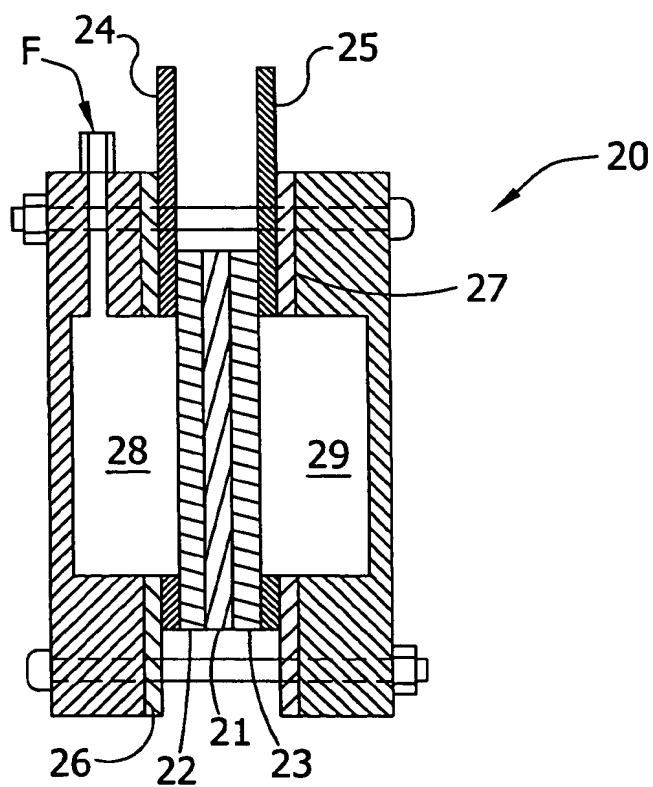


FIG. 4

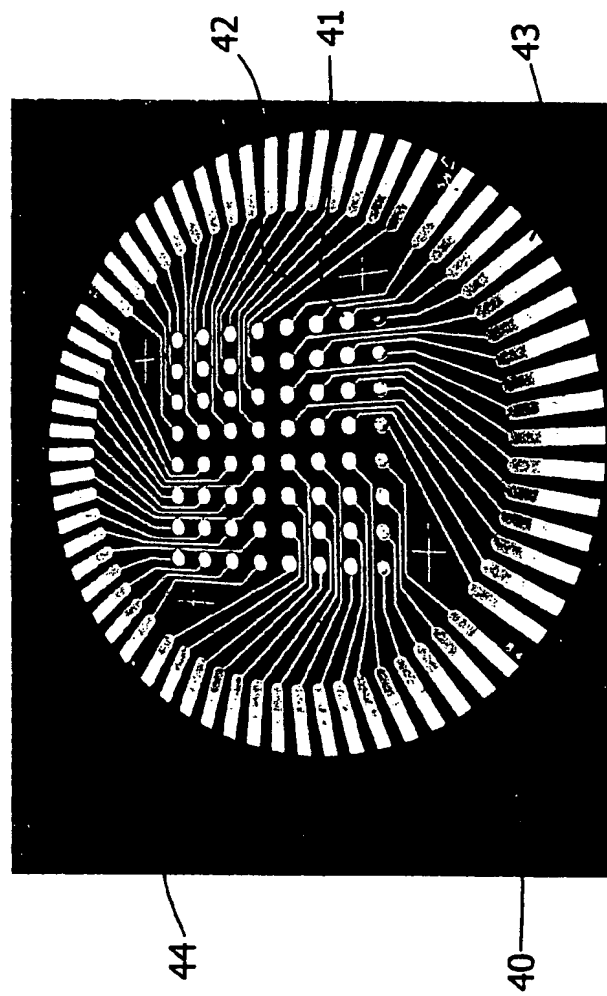
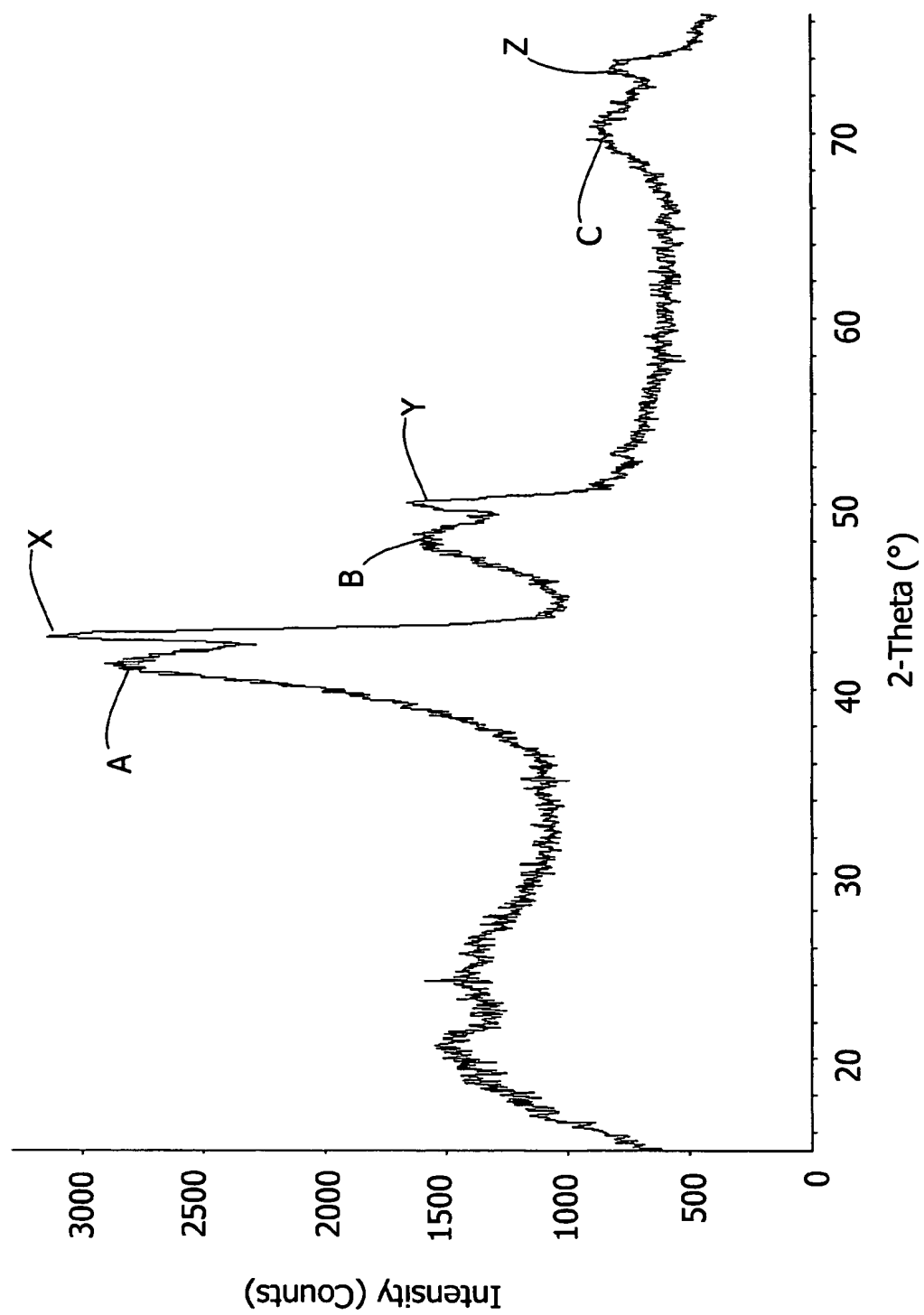


FIG. 5



APPLICATION DATA SHEET

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